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An Investigation of the Vibrational Spectra of Lignin Model Compounds

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AN INVESTIGATION OF THE VIBRATIONAL SPECTRA OF LIGNIN MODEL COMPOUNDS

A thesis submitted by

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TABLE OF CONTENTS

SUMMARY

To aid in the interpretation of the Raman spectra of lignins, the vibrational spectra of seven substituted benzenes have been investigated. The IR and Raman spectra of phenol, benzaldehyde, anisole, 4-hydroxybenzaldehyde, guaiacol, m-anisaldehyde and vanillin were assigned. Normal coordinate calculations supplemented with group frequency information and spectral data were used to assign these spectra.

Modified valence force fields were used in the normal coordinate calculations. A twelve parameter force field was developed to describe the in-plane vibrations of the phenyl ring. An eight parameter force field was developed for the out-of-plane vibrations of the ring. Twenty-two additional force constants were needed to describe the motions of the formyl group and its interactions with the ring. Seventeen force constants were necessary for the hydroxyl group, and twenty-seven for the methoxyl group. The force fields for the monosubstituted benzenes were refined using the Fletcher-Powell algorithm to produce a least squares fit of the calculated to observed frequencies. The observed frequencies of the monosubstituted benzenes were calculated with average errors of 4-6 cm^{-1}. The refined force constants were used to calculate the frequencies of the normal modes of the di- and trisubstituted benzenes. The observed frequencies of these compounds were calculated with an average error of 11-15 cm^{-1}. The reasonable fit of the observed to calculated frequencies indicates that these force constants would be transferable to more complex lignin model compounds.

The effects of mono-, di- and trisubstitution of benzene on the frequencies and intensities of the fundamental modes of benzene were noted. Of the thirty fundamental phenyl modes, six were found to be substituent sensitive in monosubstituted benzenes. Twelve were so classified for the disubstituted compounds,

as were sixteen for the trisubstituted benzene. The magnitude of the shift in frequency is dependent on the mass and chemical nature of the substituent and, in the polysubstituted compounds, on the pattern of substitution of the ring. There are few regularities in the intensities of the phenyl bands on going from mono- to trisubstituted benzenes. The intensities of these peaks can be explained to some extent based on knowledge of the form of the mode, the nature of the substituents and the pattern of substitution.

PROBLEM STATEMENT

The objective of this thesis is to investigate the vibrational spectra of lignin model compounds. Specifically the objectives are to assign the IR and Raman spectra of phenol, benzaldehyde, anisole, 4-hydroxybenzaldehyde, guaiacol, m-anisaldehyde and vanillin, noting the effect of mono-, di-, and trisubstitution on the frequencies and intensities of the fundamental modes of benzene, and to develop a force field that can be used in future investigations to aid in the interpretation of more complex lignin model compounds.

An analysis of the vibrational spectra of lignin model compounds via normal coordinate analysis will aid in the interpretation of the vibrational spectra of lignins. An understanding of the vibrational spectra of lignin will be useful in determining the in vivo structure of lignin in studies of the ultrastructure of cellulosic fibers and in studies of pulping reactions.

INTRODUCTION

Because of its role in the paper industry, many studies have been done on lignin to ascertain its structure and chemical properties. In general, these studies infer that lignin is a 3-dimensional, polydisperse, amorphous, random, branched network polymer. These conclusions are based primarily on the products that result from attempts to isolate lignin from wood. However mild the conditions for isolation, be it chemical, physical or biological, the structure of lignin is invariably altered. The conclusions reached based on these products do not necessarily apply to lignin as it occurs naturally. To determine the structure of lignin *in situ* some nondestructive means of investigating lignin is needed.

Vibrational spectroscopy is ideal for this type of analysis. Spectrometric techniques observe the interaction of the sample with electromagnetic radiation, without destroying the sample. With a Raman spectrometer the spectrum of a wood chip or a single fiber can be recorded. With a Raman microprobe the laser can be focused on a spot one micron in diameter. So the spectrum of any portion of the cell wall or middle lamella can be recorded.

IR and Raman spectra contain information about the structure of the compound under study. Not only do they contain information about the functional groups present in the samples, but they can also be used to obtain information about the orientation of the molecules in the sample. To elicit this information, these spectra must be understood. As the first step in interpreting the vibrational spectra of lignin, the aim of this thesis is to analyze the vibrational spectra of some of the simpler molecules that are considered to be lignin model compounds. An understanding of the vibrational spectra of lignin model

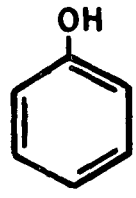
compounds will not only aid in the elucidation of the structure of native lignin, but will also be useful in studies of pulping reactions and in understanding the spectra of isolated lignins.

It is generally agreed that the basic structural unit of lignin is the phenyl propane unit. The aromatic ring may be substituted in several positions. A hydroxyl group para to the propane chain results in a coumaryl unit which is present in the lignin of grasses. Addition of a methoxyl group ortho to the hydroxyl group of the coumaryl unit produces a guaiacyl unit, which is dominant in softwood lignin. Another of the functional groups known to be present in lignin is a carbonyl group. A carbonyl group situated alpha to the ring is the most common.

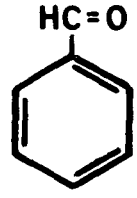
The principal focus of this investigation is the effect the addition of a substituent to the benzene ring has on the frequencies and intensities of the benzene fundamental modes. Also of interest is whether variations of intensity and frequency, with the addition of a second or third substituent, are primarily additive, or whether coupling effects arise. The influence the three functional groups, hydroxyl, methoxyl and α-carbonyl, have on the fundamental modes of benzene is to be investigated. The compounds to be analyzed are the three monosubstituted benzenes: phenol, benzaldehyde and anisole, the three disubstituted benzenes: 4-hydroxybenzaldehyde, guaiacol and m-anisaldehyde, and the trisubstituted compound, vanillin (Fig. 1).

The vibrational spectra of these compounds are analyzed using normal coordinate calculations supplemented with known group frequency information. The study of these compounds is broken into four levels: benzene, the monosubstituted benzenes, the disubstituted derivatives and the trisubstituted compound.

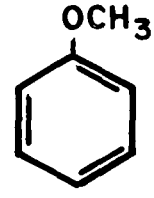
This progression of compounds enables the information acquired from the simplest systems to be applied to the interpretation of the more complex molecules.



PHENOL

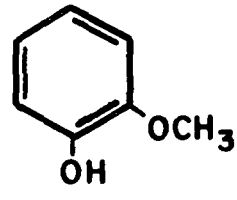


BENZALDEHYDE

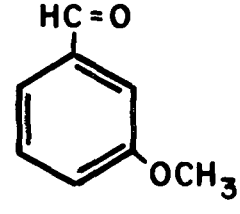


ANISOLE

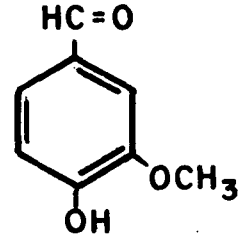
4-HYDROXYBENZALDEHYDE



GUAIACOL



M-ANISALDEHYDE



VANILLIN

Figure 1. Structures for the compounds under investigation.

To carry out a normal coordinate analysis, a force field for the molecule is needed (a discussion of normal coordinate calculations is included in Appendix I). Benzene and substituent force fields are to be used to construct the force fields for the initial calculations of the fundamental frequencies of

the model compounds. So a benzene force field is needed. The development of the benzene force field to be used in this investigation is presented in Chapter I.

To initially calculate the vibrational frequencies of the monosubstituted benzenes, a zeroth approximation force field is constructed from the benzene force field and the appropriate substituent force field. No force constants are added to this force field to account for interactions between the phenyl and substituent groups. The potential energy distribution calculated using this force field is used to assign the vibrational spectra of the monosubstituted benzenes. The zeroth approximation force field is not refined.

The modified valence force fields (MVFF) are then constructed from the zeroth approximation force fields. In addition to the benzene and substituent force constants, force constants are included for interactions between the phenyl and substituent groups. The initial modified valence force fields are refined to improve the fit of the calculated to the observed frequencies. Two strategies are used for these refinements. One is to refine the full field simultaneously, an unconstrained refinement. The other is to refine the substituent force constants, holding the phenyl force constants constant, then to refine the phenyl force constants, constraining the substituent force constants to their refined values. The refined force fields are evaluated based on the fit of the calculated to observed frequencies, on the values of the force constants and on the potential energy distribution calculated using the force field. The results may indicate a need to alter the assignment of the observed frequencies or to change the force field in some way. If so, the changes are made and the refinements are repeated.

Modified valence force fields are developed for each of the monosubstituted benzenes. Since the force fields are developed to be transferred to the force fields for the di- and trisubstituted benzenes, the phenyl portions of the MVFF's have the same form for all three compounds (i.e., the internal coordinate and force constant definitions for the phenyl ring are the same for each molecule). To generalize the phenyl force fields, the phenyl portions of the force fields for phenol, benzaldehyde and anisole are refined to the observed frequencies of all three compounds simultaneously. The phenyl force constants that result from this refinement are used in the calculations of the fundamental frequencies of the di- and trisubstituted benzenes.

The development of the force fields for the monosubstituted benzenes and the refinements of these force fields are presented in Chapter II. The assignments of the phenyl modes of the monosubstituted benzenes are compared to each other and to those of benzene to ascertain the effect of monosubstitution, in general, and of the hydroxyl, formyl and methoxyl substituents, in particular, on the fundamental modes of benzene. The assignment of the normal modes and their comparison are also discussed in Chapter II.

The refined phenyl and substituent force fields are then used to calculate the frequencies of the normal modes of the disubstituted benzenes. The phenyl force constants from the joint refinement and the substituent force constants from the individual refinements are used in these calculations. Refinements of the modified valence force field for 4-hydroxybenzaldehyde demonstrated that refinement of the modified valence force fields for the disubstituted benzenes does not significantly improve the fit of the calculated to observed frequencies, nor does it improve the potential energy distributions. So the MVFF's for

the disubstituted benzenes are not refined. The normal coordinate calculations are used to interpret the vibrational spectra of 4-hydroxybenzaldehyde, guaiacol and m-anisaldehyde. The frequencies and intensities of the phenyl modes of these compounds are compared with those of benzene and the monosubstituted benzenes to discern the effect of a second substituent on these modes. The normal coordinate calculations and the assignments of the spectra of the disubstituted benzenes are discussed in Chapter III.

The phenyl and substituent force constants are used to calculate the fundamental modes of the trisubstituted benzene, vanillin. In an effort to improve the transferability of the phenyl force constants the phenyl portions of the MVFF's for the disubstituted benzenes are simultaneously refined to the observed frequencies of all three disubstituted compounds. This refinement does not significantly change the force constants or the fit of the calculated to the observed frequencies. The normal coordinate calculations are used to interpret the IR and Raman spectra of vanillin. The frequencies and intensities of the phenyl modes of vanillin are compared with those of the other substituted benzenes to ascertain the influence of a third substituent on these modes. The normal coordinate calculations and the assignment of the vibrational spectra of vanillin are discussed in Chapter IV.

Knowledge of the effect these substituents and the different patterns of substitution have on the phenyl modes will facilitate the identification of these modes in the spectra of lignin. What is known about the vibrational spectra of lignin and what can be said about the spectra of lignin based on the results of this investigation is reviewed in Chapter V.

CHAPTER I. DEVELOPMENT OF A MODIFIED VALENCE FORCE FIELD FOR BENZENE

INTRODUCTION

The vibrational spectra of the lignin model compounds are assigned using normal coordinate calculations supplemented with group frequency information. The data required to perform a normal coordinate analysis include the masses of the atoms, the structure of the molecule, internal coordinate definitions, a force field for the molecule and the values of the force constants. Benzene and substituent force fields are to be used to construct the force fields for the initial calculations of the fundamental frequencies of the model compounds. So, an initial benzene force field is needed. The development of the benzene force field for use in this investigation is presented in this Chapter. The various internal coordinates and a representative selection of the force fields used for normal coordinate analyses of benzene are reviewed.

Another concern of this investigation is the effect substitution of the aromatic ring has on the fundamental modes of benzene. Hence it is necessary to know the frequencies and forms of these modes in benzene. The accepted assignments and forms of the fundamental modes of benzene are presented in this chapter.

LITERATURE REVIEW

ANALYSIS OF THE VIBRATIONAL SPECTRA

The vibrational spectra of benzene have been extensively studied due to the importance of benzene as an organic material and to the high symmetry of the benzene molecule. The symmetry of this molecule facilitated early interpretations of its vibrational spectra.

Benzene has a planar structure (1), with the carbon and hydrogen atoms at the corners of concentric regular hexagons, their axes aligned. Due to this regular structure, benzene belongs to the D_{6h} point group. (The significance of this classification is discussed in most treatments of the chemical applications of group theory. An overview of the applications of group theory to vibrational spectroscopy is included in Appendix I.) The in-plane and out-of-plane modes of benzene are orthogonal, so these two problems can be considered separately. The $2N-3$ in-plane modes and the $N-3$ out-of-plane modes can be divided according to their behavior with respect to the other symmetry elements present in the molecule. The twenty-one in-plane modes divide into symmetry species $2A_{1g} + A_{2g} + 4E_{2g} + 2B_{1u} + 2B_{2u} + 3E_{1u}$. The nine out-of-plane modes separate into species $2B_{2g} + E_{1g} + A_{2u} + 2E_{2u}$. The E symmetry species are doubly degenerate, i.e., each refers to two fundamental modes with the same frequency. The selection rules specify the modes of species $A_{1g} + E_{1g} + E_{2g}$ to be Raman active, and those of species $A_{2u} + E_{1u}$ to be infrared active. The remaining modes, $A_{2g} + B_{1u} + B_{2u} + B_{2g} + E_{2u}$, are inactive in both IR and Raman spectra. Due to the center of inversion, the modes that are active in the IR are not active in the Raman, and vice versa. This is known as the mutual exclusion rule. The Raman lines of the modes of species A_{1g} will be polarized.

The frequencies of the fundamental modes of benzene are well established. They have been assigned using Raman depolarization ratios, isotopic studies and normal coordinate calculations. The forms of the normal modes are also known. The frequencies of the normal modes of benzene are listed in Table I. Depictions of the normal vibrations of benzene are presented in Fig. 2. There are several different numbering systems used to identify the benzene modes. The one used in

Table I and Fig. 2 is known as the Wilson numbering system (2) and will be used throughout this thesis.

TABLE I

THE NORMAL MODES OF BENZENE[a]

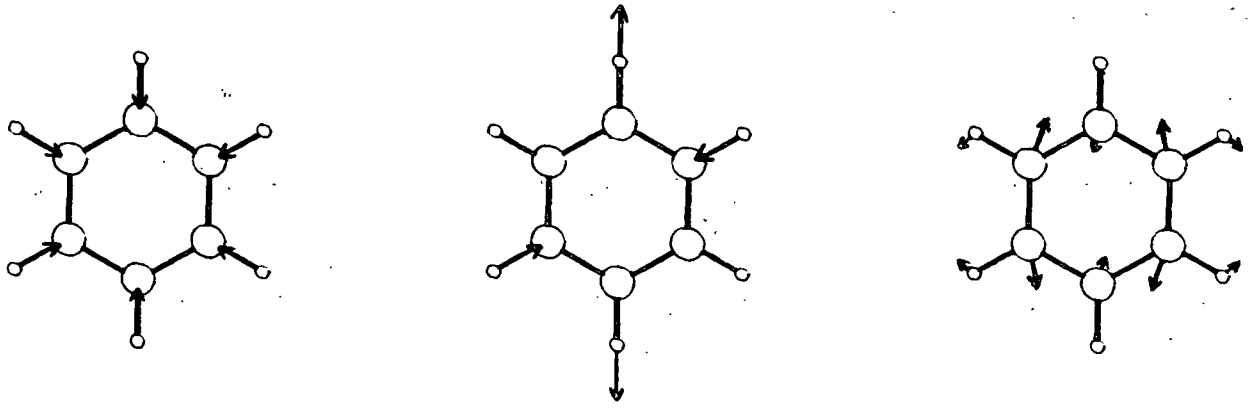
Mode	Symmetry Species	Wavenumber, cm^{-1}	IR	Raman	Assignment
1	A_{1g}	999	ia	p	ip breathing, in-phase
2		3073	ia	p	ip CH stretch
3	A_{2g}	1350	ia	ia	ip CH bend
4	B_{2g}	703	ia	ia	oop ring deformation
5		989	ia	ia	oop CH bend
6	E_{2g}	606	ia	dp	ip ring deformation
7		3056	ia	dp	ip CH stretch
8		1599	ia	dp	ip CC stretch
9		1178	ia	dp	ip CH bend
10	E_{1g}	849	ia	dp	oop CH bend
11	A_{2u}	670	a	ia	oop CH bend
12	B_{1u}	1010	ia	ia	ip breathing, out-of-phase
13		3057	ia	ia	ip CH stretch
14	B_{2u}	1309	ia	ia	ip CC stretch
15		1152	ia	ia	ip CH bend
16	E_{2u}	404	ia	ia	oop ring deformation
17		966	ia	ia	oop CH bend
18	E_{1u}	1037	a	ia	ip CH bend
19		1482	a	ia	ip CC stretch
20		3064	a	ia	ip CH stretch

[a]Inactive (ia), active (a), polarized (p), depolarized (dp), in-plane (ip), out-of-plane (oop).

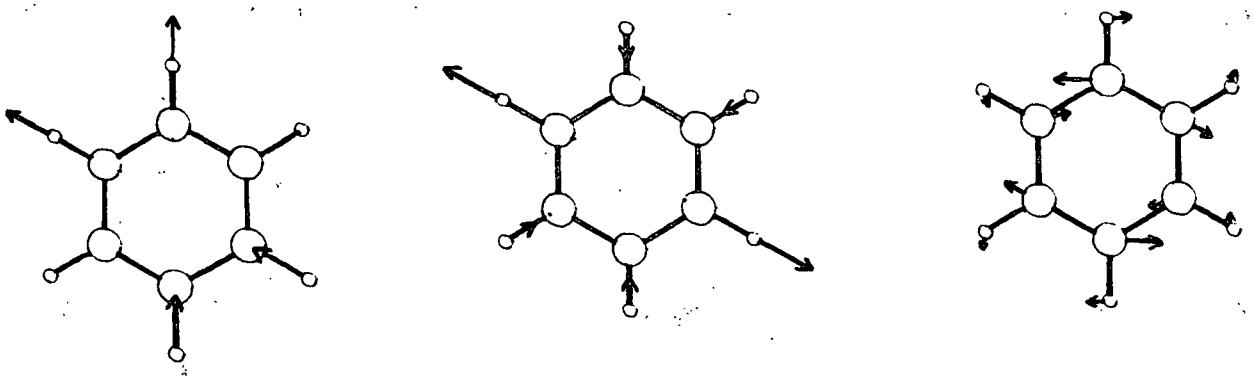
NORMAL COORDINATE ANALYSES

In this investigation, as in most normal coordinate calculations, Wilson's GF matrix formalism (3) is used to set up the vibrational problem. Normal coordinate calculations are discussed in detail in the text Molecular Vibrations by Wilson, Decius and Cross (3), and are reviewed in many of the texts on vibrational spectroscopy [e.g., (4,5)]. A limited discussion of normal coordinate calculations is included in Appendix I.

Normal Mode 2 = 3072 cm^{-1} Normal Mode 7B = 3057 cm^{-1} Normal Mode 8A = 1599 cm^{-1}



Normal Mode 20B = 3064 cm^{-1} Normal Mode 7A = 3056 cm^{-1} Normal Mode 8B = 1599 cm^{-1}



Normal Mode 20A = 3070 cm^{-1} Normal Mode 13 = 3056 cm^{-1} Normal Mode 19A = 1482 cm^{-1}

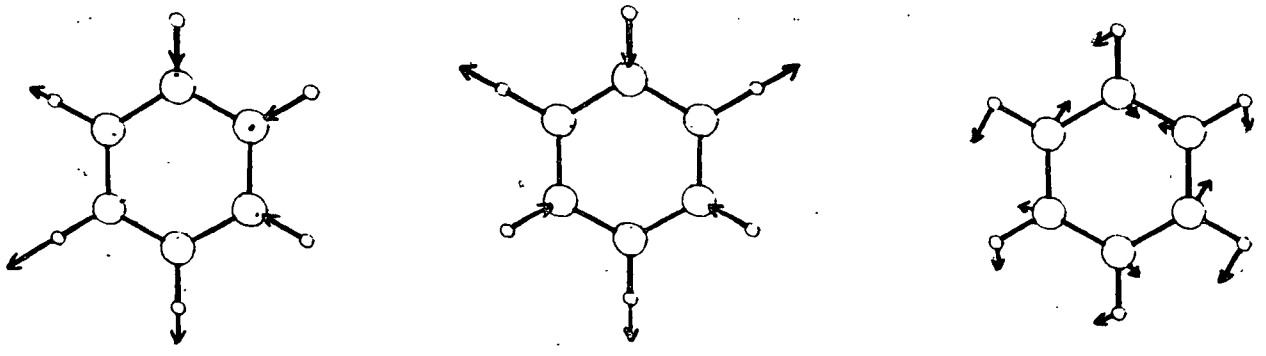
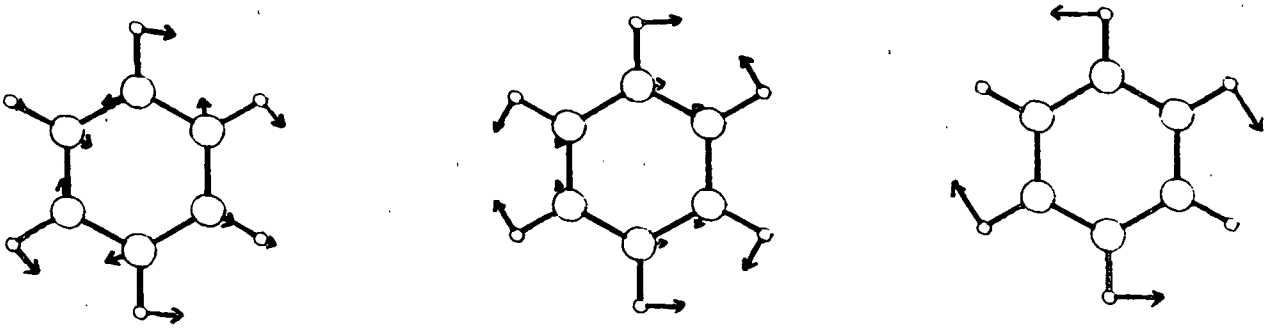
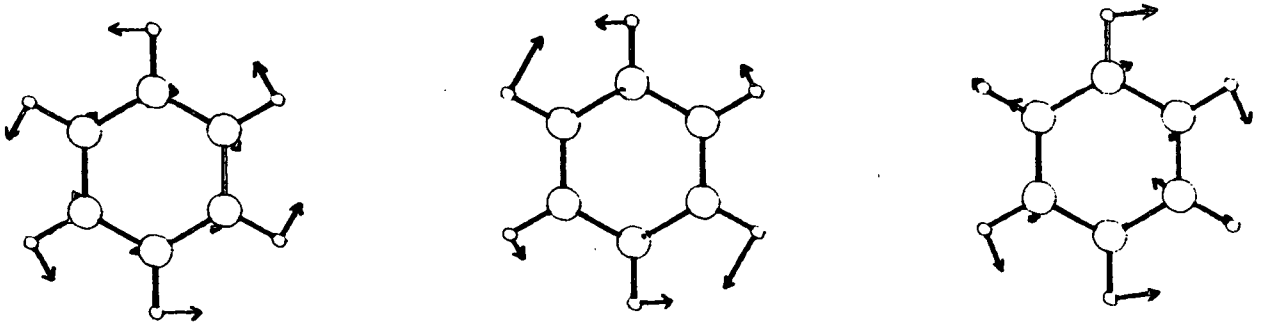


Figure 2a. In-plane vibrations of benzene.

Normal Mode 19B = 1482 cm^{-1} Normal Mode 15 = 1152 cm^{-1} Normal Mode 9B = 1176 cm^{-1}



Normal Mode 3 = 1350 cm^{-1} Normal Mode 9A = 1164 cm^{-1} Normal Mode 18B = 1037 cm^{-1}



Normal Mode 14 = 1309 cm^{-1} Normal Mode 18A = 1037 cm^{-1} Normal Mode 12 = 1010 cm^{-1}

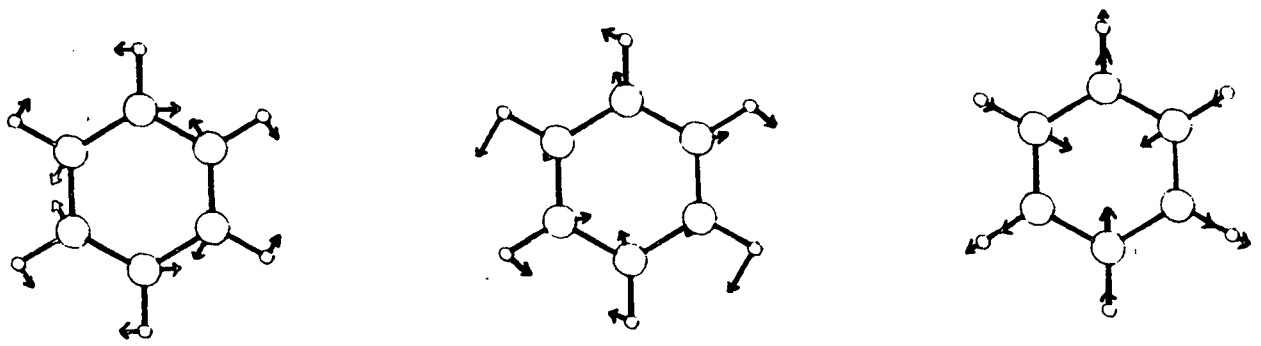


Figure 2a (Continued). In-plane vibrations of benzene.

Normal Mode 1 = 993 cm^{-1} Normal Mode 6A = 606 cm^{-1} Normal Mode 6B = 606 cm^{-1}

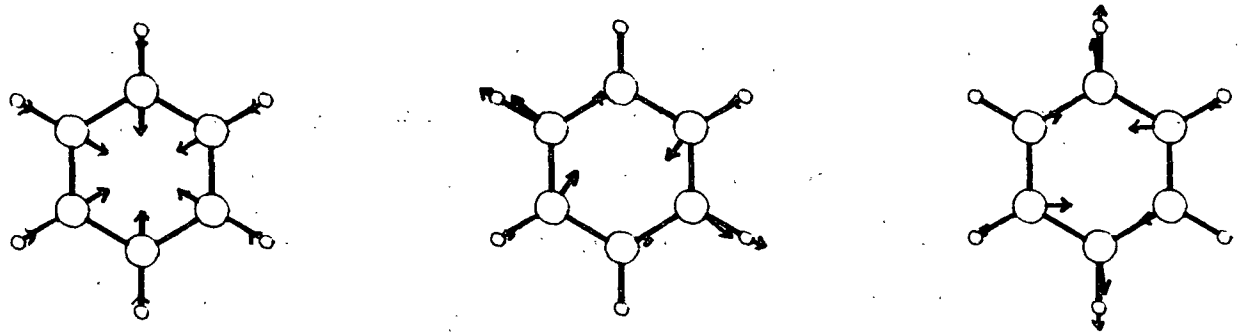
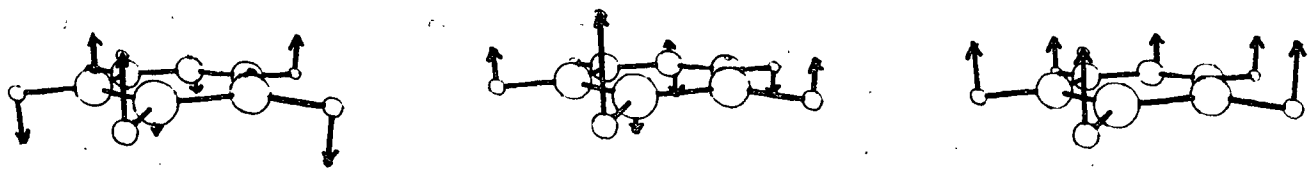
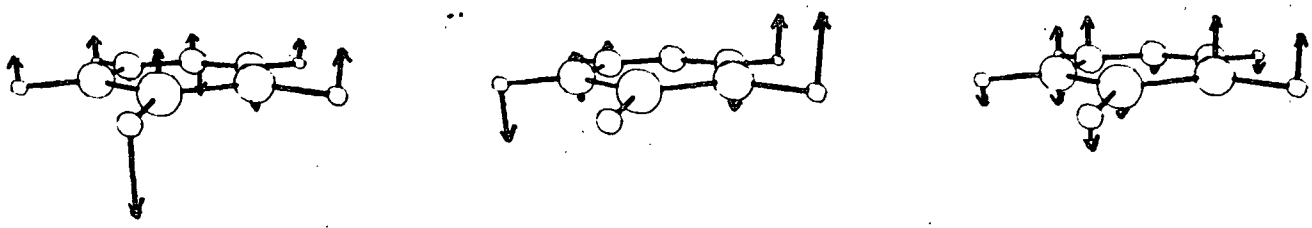


Figure 2a (Continued). In-plane vibrations of benzene.

Normal Mode 5 = 990 cm^{-1} Normal Mode 10A = 850 cm^{-1} Normal Mode 11 = 672 cm^{-1}



Normal Mode 17A = 968 cm^{-1} Normal Mode 10B = 850 cm^{-1} Normal Mode 16A = 404 cm^{-1}



Normal Mode 17B = 968 cm^{-1} Normal Mode 4 = 704 cm^{-1} Normal Mode 16B = 404 cm^{-1}

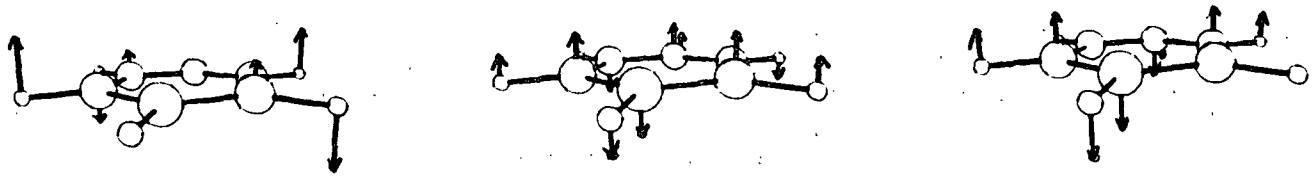


Figure 2b. Out-of-plane vibrations of benzene.

Briefly, the potential energy matrix is constructed from information about the atomic masses, molecular structure, and the internal coordinates used to describe the molecule. The kinetic energy matrix is the matrix of the force constants for the molecule. The eigenvalues of the product of the potential and kinetic energy matrices are related to the normal frequencies of the vibrations of the molecule. The eigenvectors of the product matrix are the normal modes of vibration of the molecule. So the information required to perform a normal coordinate analysis includes: the masses of the atoms, the structure of the molecule, the internal coordinate definitions, the force field and the values of the force constants for the molecule.

The symmetry of benzene made it a prime candidate for normal coordinate studies before the advent of the computer. Though benzene has thirty degrees of vibrational freedom the secular equation can be factored, using symmetry considerations, so that the largest block is a 4 x 4 matrix. Hence there have been many attempts to develop a general valence force field for benzene. As well, there have been several attempts to develop force fields transferable to substituted benzenes. Many of these analyses are reviewed by Varsanyi (6).

Internal Coordinates

In-plane Coordinates

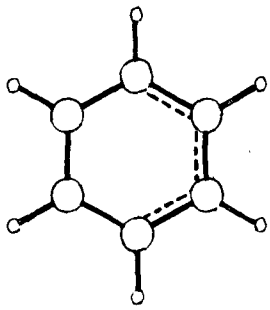
The internal coordinates for the in-plane vibrations of benzene can be defined two ways. One set is composed of six CC bond stretches, six CH bond stretches, six CCC angle bends and twelve CCH angle bends. This set of thirty internal coordinates includes nine redundant coordinates. Six of these redundancies arise from including all three angles about each carbon atom. The remaining three redundancies are a result of the ring structure; the necessity

of ring closure imposes three restrictions on the possible normal vibrations. The other set of internal coordinates also starts with six CC stretches, six CH stretches and six CCC deformations, but is completed with six linear combinations of the CCH angle deformations. The linear combination of the CCH angle bends can also be considered to be the angle between the CH bond and the exterior bisector of the CCC angle. Only the three redundancies due to the ring structure are present in this set of internal coordinates. This second set is more commonly used, especially if the problem is to be factored. The ring redundancies are eliminated after the potential and kinetic energy matrices have been factored.

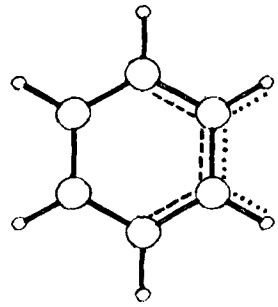
Out-of-plane Coordinates

There are also two different sets of internal coordinates used to describe the out-of-plane problem. Both types of internal coordinates include the six out-of-plane hydrogen wags and the six torsions about the CC bonds. It is the definition of the torsional coordinates that differs. One set defines the torsions as simply the change in the angle between the C_{i-1}, C_i, C_{i+1} and C_i, C_{i+1}, C_{i+2} planes. These are known as delta coordinates. The other defines the torsions to be a linear combination of the change in the angle between the C_{i-1}, C_i, C_{i+1} and C_i, C_{i+1}, C_{i+2} planes and the change in the angle between the H_i, C_i, C_{i+1} and C_i, C_{i+1}, H_{i+1} planes, and are known as phi coordinates (Fig. 3). Phi coordinates were first suggested by Bell (7) because there was no physical justification for neglecting the relative twist of the C_iH_i and C_{i+1} H_{i+1} bonds, "especially since the hydrogen atoms will usually move through greater distances than the carbon atoms." Whiffen (8) further rationalized that the force opposing twisting arises from the incomplete sideways overlap of the p_z atomic orbitals on adjacent C atoms, and that the directions of these orbitals are defined by

the positions of both the carbon and hydrogen atoms. Both delta and phi internal coordinates include three redundant coordinates arising from the cyclical structure of benzene. Again, these are generally removed after the potential and kinetic energy matrices have been factored.



Delta torsional coordinates



Phi torsional coordinates

Figure 3. Definition of the torsional internal coordinates.

Force Fields

A general quadratic force field (GQFF) for benzene, as for any but the simplest polyatomic molecules, cannot be determined. There are many more force constants than there are observed frequencies. Hence there have been a variety of approximate force fields proposed. The first major calculations of the vibrational spectra of benzene were performed by Crawford and Miller (9). The force constants were calculated from information available about the vibrational spectra; no refinement of these constants was performed. More recently, refinement techniques have freed force field developments somewhat from the constraint of exact solution of the secular equation. This liberation resulted in a variety

of approximate force fields being developed, from Scherer's nine parameter in-plane force field (10,11), to Painter's twenty-two parameter in-plane force field (12,13).

In-plane Force Fields

Crawford and Miller (9) took advantage of a more complete assignment of the vibrational spectra of benzene to carry out the first major normal coordinate treatment of this molecule. Their calculations were based on a modified GQFF in which various interaction constants were somewhat arbitrarily set equal to zero. The factored in-plane GQFF contained twenty-six valence force symmetry constants VFSC [the VFSC are linear combinations of the valence force constants (VFC), created when the force field is factored] six of which were assumed to be zero. The twenty nonzero VFSC calculated the fourteen in-plane frequencies with an average error of 6 cm^{-1} (the error is the difference between an observed and calculated frequency). Only eight of the thirty-three valence force constants (VFC) were determined from the VFSC (there are fewer VFSC than VFC, so even if all of the VFSC could be determined, it would not be possible to calculate all of the VFC).

Whiffen (8) developed a slightly different force field for benzene by modifying Crawford's analysis. Whiffen reduced the number of VFC to twenty-six by setting to zero those expected to be small. Furthermore, seven of both the twenty-six VFC and twenty-six VFSC were assumed to be zero. The nineteen non-zero VFC calculated the in-plane frequencies with an average error of 4 cm^{-1}.

The above force fields were developed by adjusting the force constants to give the best fit to the available data for each symmetry species in turn. Coupling refinement techniques to the solution of the secular equation made

possible the simultaneous refinement of all force constants to the observed data. New force field developments ranged from those aiming for the minimum number of force constants needed to adequately reproduce all of the observed data, to those seeking to find all force constants necessary to accurately calculate the vibrational frequencies of benzene. Duinker and Mills (14) developed a thirteen (VFC) parameter modified valence force field for the in-plane vibrations of benzene. This force field calculated the observed frequencies with an average error of 6 cm^{-1}. Scherer (10,11), investigating the vibrational spectra of chlorobenzenes, developed a nine parameter modified valence force field for benzene. This force field, which was transferable to the chlorobenzenes, was used to calculate the experimental frequencies with an average error of 12 cm^{-1}. Neto, et al. (15) developed a ten parameter force field to describe the planar modes of benzene. This force field was developed in conjunction with similar force fields for naphthalene and anthracene. The fourteen in-plane frequencies were calculated with an average error of 8 cm^{-1}. Painter, et al. (12,13) sought a "physically improved" potential function and came up with a twenty-two parameter modified valence force field. This force field calculated the observed frequencies with an average error of 4 cm^{-1}. Neto and Scherer used the set of thirty in-plane internal coordinates for their calculations, the others used the twenty-four member set.

Out-of-plane Force Fields

As with the in-plane calculations, a variety of force fields have been used to describe the benzene out-of-plane problem. The fields have ranged from modified GQFF's consisting of nine valence force constants, to a modified valence force field of just two valence force constants. A full GQFF would

comprise eleven valence force constants. However, there are only nine out-of-plane frequencies for benzene. Therefore, only nine force constants can be calculated without refinement of the force constants. The GQFF can be factored. The resulting matrices contain eight VFSC. Miller and Crawford (16) and Whiffen (8) each calculated the eight VFSC of the out-of-plane force field for benzene. Whiffen also calculated eight of the VFC, setting three to zero. The force fields developed by Miller and Crawford and by Whiffen calculated the observed frequencies with average errors of 8 cm^{-1} and 4 cm^{-1}, respectively. Kakiuti (17) developed a modified valence force field based on five valence force constants. This force field calculated the observed frequencies with an average error of 12 cm^{-1}. Painter's potential function used eight valence force constants to calculate the observed frequencies with an average error of 1 cm^{-1} (12,13). Of these force fields only Kakiuti used delta torsional coordinates; the others used phi torsional coordinates for their calculations.

VIBRATIONAL ANALYSIS

CALCULATIONS

To construct a force field for benzene derivatives, it is first necessary to develop an appropriate benzene force field. Two in-plane and two out-of-plane benzene force fields were investigated. The two in-plane force fields were based on those developed by Painter (12,13) and by Neto (15). The out-of-plane force fields were developed using force fields created by Painter (12,13) and Kakiuti (17). The calculations presented by each of these authors were repeated, then refined for use in this thesis.

Painter (13) used the accepted structure for benzene and the set of twenty-four in-plane internal coordinates to set up the kinetic energy matrix. The

potential energy matrix was formulated in terms of a modified valence force field. The in-plane force field comprised twenty-two force constants. The definitions of these force constants along with their values are listed in Table II. The diagonal force constants were given initial values from La Lau and Snyder's benzene force field (18) and the interaction constants were set equal to zero. Painter refined this force field to the observed frequencies of $^{12}C_6H_6$, $^{12}C_6D_6$, and $^{13}C_6H_6$ by a damped least squares method.

TABLE II

IN-PLANE FORCE CONSTANTS[a] FOR BENZENE

Force Constant	Coordinate	Initial		Final		
		Painter	Neto	22 VFC	11 VFC	12 VFC
1	CC	7.0067	6.433	7.006	6.456	6.473
2	CH	5.0220	5.055	5.042	5.101	5.086
3	CCH	0.9912[b]	0.511	0.988	0.508	0.506
4	CCC	1.4612	0.934	1.454	0.920	0.940
5	o-CC,CC	0.6432	0.750	0.634	0.784	0.797
6	m-CC,CC	-0.5908	-0.316	-0.610	-0.336	-0.330
7	p-CC,CC	0.6192	0.342	0.605	0.312	0.255
8	o-CC,CCH	-0.3838	0.174	-0.384	0.176	0.154
9	o'-CC,CCH	0.3838	-	0.384	-	-
10	m-CC,CCH	-0.0803	-	-0.078	-	-
11	m'-CC,CCH	0.0803	-	0.077	-	-
12	p-CC,CCH	0.1441	-	0.148	-	-
13	p'-CC,CCH	-0.1441	-	-0.148	-	-
14	CC,CCC	0.3439	0.164	0.352	0.180	0.184
15	CC,CH	-0.1150	-	-0.065	-	-
16	o-CH,CH	0.0130	0.017	0.017	0.017	0.014
17	o-CCC,CCC	0.0847	-0.045	0.078	-0.063	-0.048
18	o-CCC,CCH	-0.1421	-	-0.136	-	-
19	o'-CCC,CCH	0.1427	-	0.137	-	-
20	o-CCH,CCH	0.0254	-	0.024	-	-0.002
21	m-CCH,CCH	-0.0014	-	-0.0001	-	-
22	p-CCH,CCH	-0.0370	-	-0.0346	-	-
Average error, %		0.221	0.473	0.213	0.471	0.247

[a]Units: stretch-stretch, mdyne/Å; stretch-bend, mdyne/rad; bend-bend, mdyne Å/rad^2.

[b]Different normalization constants for the CCH angle deformations were used in this work than those used by Painter. These force constants have been adjusted accordingly.

Neto (15) used the set of thirty in-plane internal coordinates and the standard geometry for benzene to calculate the G matrix. The F matrix was based on a modified valence force field. This benzene field included eleven valence force constants. The definitions and final values of these force constants are listed in Table II. Analogous force fields were defined for naphthalene and anthracene, requiring a total of thirty-four force constants for all three molecules. Neto simultaneouly refined these three force fields to their observed frequencies by a steepest descent method.

Kakiuti (17) defined the out-of-plane problem using delta coordinates. A modified valence force field was used to set up the potential energy matrix. This force field consisted of five valence force constants. The definitions of these force constants are included in Table III. Initial values of these force constants were from Miller and Crawford's out-of-plane force field (16). Kakiuti used a least squares method to refine the initial force field to the observed frequencies of C_6H_6 and C_6D_6.

TABLE III

OUT-OF-PLANE FORCE CONSTANTS[a] FOR BENZENE

Force Constant	Coordinate	Initial		Final		
		Painter	Kakiuti	8 VFC	6 VFC	7 VFC
1	Wag	0.3237	0.378	0.3209	0.491	0.3211
2	Torsion	0.2380[b]	0.111	0.2476	0.455	0.2384
3	o-Wag,wag	0.0184	-0.060	0.0176	-0.098	0.0192
4	m-Wag,wag	-0.0235	--	-0.0219	--	-0.0237
5	p-Wag,wag	-0.0227	--	-0.0223	--	-0.0233
6	o-Tor,tor	-0.0776	-0.046	-0.0716	-0.035	-0.0787
7	Tor,wag	-0.0386	-0.109	-0.0382	-0.256	-0.0372
8	Tor,wag	0.0372	0.109[c]	0.0368	0.256[c]	0.0372[c]
Average error, %		0.174	1.60	0.178	0.326	0.016

[a]Units: mdyne Å/rad^2.

[b]A different normalization constant for the torsional coordinates was used in this work than that used by Painter. These force constants have been adjusted accordingly.

[c]Kakiuti defined force constant 8 to be equal to minus the value of force constant 7. Only five independent force constants were defined.

Painter (12) used phi coordinates to set up his out-of-plane calculations. A modified valence force field comprising eight valence force constants was employed to calculate the nine out-of-plane vibrational frequencies of benzene. Initial values of the diagonal force constants were from La Lau and Snyder's benzene force field (18). The interaction constants were set equal to zero. Painter refined this field to minimize the difference between the calculated and observed frequencies of $^{12}C_6H_6$, $^{13}C_6H_6$ and $^{12}C_6D_6$ by a damped least squares method. The definitions of the force constants and their values are listed in Table III.

To develop an in-plane benzene force field for use in this investigation both Painter's and Neto's calculations were duplicated. Once duplicated these two force fields were refined using the Fletcher-Powell refinement technique to minimize the difference between the calculated and observed frequencies. Values for the experimental frequencies of benzene were taken from Painter's work (12). The resulting force constants are included in Table II. Two modifications of Painter's force field were also evaluated (19). Neither of these modifications were better able to calculate the observed frequencies than the refinement of Painter's original force field.

The force field used to calculate the frequencies of the out-of-plane modes of benzene was developed in a similar fashion. The force fields of Kakiuti and Painter were duplicated and subsequently refined. The Fletcher-Powell refinement procedure was used. The refined force constants are displayed in Table III. Several modifications of these force fields were also evaluated (20). None of these modifications resulted in a better fit of calculated to observed frequencies.

EVALUATION OF SOLUTION

Using the in-plane force fields based on Painter's (12,13) (twenty-two parameter) and Neto's (15) (eleven parameter) force fields and the out-of-plane force fields based on Painter's and Kakiuti's (17) force fields, the observed frequencies are calculated well. The respective average errors are 3.43 cm^{-1} or 0.213%, 8.86 cm^{-1} or 0.471%, 1.33 cm^{-1} or 0.178% and 2.61 cm^{-1} or 0.326%. However, accurate calculation of the experimental frequencies is not the sole criterion used to evaluate force fields. In addition to being able to duplicate the observed frequencies with minimal error, the values of the force constants and the potential energy distribution must be reasonable. In this investigation it is also desired that there be a minimum number of force constants, and that the force field be transferable to substituted benzene derivatives.

To be considered "reasonable" the values of the force constants should agree with the values of analogous force constants found in force fields for similar (or equivalent) molecules or groupings. Inspection of the force constants listed in Tables II and III show that the benzene force constants resulting from the refinements are similar to Painter's and Neto's benzene force constants and therefore meet this requirement. A potential energy distribution shows the contribution of each internal coordinate to each normal mode. A "reasonable" potential energy distribution will comprise assignments of the normal frequencies that agree with assignments made on the basis of group frequency data, deuteration studies, and information gleaned from the vibrational spectra of the compound (e.g., Raman depolarization ratios, and IR and Raman band shapes). The potential energy distributions calculated with the benzene force fields developed in this investigation give such an assignment of the normal frequencies of benzene (Tables IV and V).

The condition that there should to be a minimum number of force constants arises from the fact that this force field is being developed as a tool to aid in the correct interpretation of the vibrational spectra of the molecules under consideration, not as a unique potential energy function for this molecule. Considering the approximations involved in the use of a harmonic potential and of uncorrected experimental frequencies, the inclusion of numerous interaction constants in the field appears to be a nugatory complication. Based on this preference and on calculations for phenol, the benzene in-plane force field developed from the Neto in-plane force field is chosen to be the basis for constructing the in-plane force fields for the substituted benzene derivatives.

TABLE IV

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE IN-PLANE VIBRATIONS OF BENZENE

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
3073	3071	2	0.06	CH(98)
3064	3065	-1	-0.03	CH(99)
3064	3065	-1	-0.03	CH(99)
3057	3057	0	0.02	CH(99)
3056	3057	-1	-0.02	CH(99)
3056	3055	1	0.02	CH(99)
1599	1599	0	0.02	CC(79) CCH(26)
1599	1599	0	0.02	CC(79) CCH(26)
1482	1483	-1	-0.05	CCH(64) CC(36)
1482	1483	-1	-0.05	CCH(64) CC(36)
1350	1349	1	0.05	CCH(101)
1309	1309	0	0.03	CC(123) CCH(46)
1178	1178	0	-0.00	CCH(57) CC(46)
1178	1165	13	1.08	CCH(77) CC(14)
1152	1165	-13	-1.15	CCH(77) CC(14)
1037	1035	2	0.23	CC(47) CCH(39)
1037	1035	2	0.23	CC(47) CCH(39)
1010	1012	-2	-0.22	CCC(72) CCH(19)
999	995	4	0.43	CC(84)
606	601	5	0.87	CCC(66) CCH(18) CC(12)
606	601	5	0.86	CCC(66) CCH(18) CC(12)
Average Error		3	0.26	

[a]The internal coordinates are the CC stretches (CC), the CH stretches (CH), the CCH bends (CCH) and the CCC bends (CCC).

TABLE V

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE OUT-OF-PLANE VIBRATIONS OF BENZENE

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
989	989	0	0.04	WAG(96) TOR(32)
966	966	0	-0.00	WAG(92) TOR(28)
966	966	0	-0.00	WAG(92) TOR(28)
849	849	0	-0.01	WAG(81) TOR(20)
849	849	0	-0.01	WAG(81) TOR(20)
703	703	0	0.03	WAG(36) TOR(32)
670	670	0	0.01	WAG(111)
404	404	0	-0.03	TOR(51) WAG(19)
404	404	0	-0.03	TOR(51) WAG(19)
Average Error		0	0.02	

[a]The internal coordinates for the out-of-plane vibrations of benzene are wags (WAG) and torsions (TOR).

The out-of-plane force field based on the Painter out-of-plane force field is selected to be the basis for constructing the out-of-plane force fields for the model compounds. This is chosen over the simpler Kakiuti force field because it is found to give a better potential energy distribution on refinement. Also, based on the arguments put forth by Whiffen (8), the phi coordinates of the Painter force field are thought to better describe the system. A simplification was made to the Painter out-of-plane force field for use in this investigation. Force constant 8 (the interaction constant between wag_{i+1} and $torsion_i$) was set equal to the negative of force constant 7 (the interaction constant between wag_i and $torsion_i$). This relationship is expected due to symmetry considerations (12).

Calculations of the vibrational spectrum of phenol indicated the need for interaction constants between the CCH angle deformations in the in-plane force

field for benzene to satisfy the condition of transferability desired in this study. Ortho, meta, and para interaction constants between these coordinates were evaluated in the phenol force field. Addition of the ortho interaction constant was sufficient to accurately calculate the potential energy distribution for phenol. This force constant was added to the in-plane benzene force field. On refinement, this force field contained reasonable force constants and accurately calculated both the observed frequencies and the potential energy distribution. This force field is used as the basis for the force fields for the in-plane vibrations of the monosubstituted benzenes.

SUMMARY

The final force field used to calculate the frequencies of the in-plane modes of benzene consists of twelve force constants and calculates the twenty-one frequencies with an average error of 2.56 cm^{-1} or 0.26%. The final force field used to calculate the frequencies of the out-of-plane modes of benzene includes seven force constants and calculates the nine frequencies with an average error of 0.20 cm^{-1} or 0.02%. The force constant definitions and values are listed in Tables II and III. The potential energy distributions calculated using these force fields are presented in Tables IV and V.

CHAPTER II. AN ANALYSIS OF THE VIBRATIONAL SPECTRA OF THE MONOSUBSTITUTED BENZENES: PHENOL, BENZALDEHYDE, AND ANISOLE

INTRODUCTION

To aid in the understanding of the vibrational spectra of lignin, the vibrational spectra of lignin model compounds are interpreted. These spectra are assigned using normal coordinate analyses supplemented with group frequency information. The crux of a normal coordinate calculation is the development of a potential energy matrix, or force field. In this investigation, initial force fields for the monosubstituted benzenes are composites of phenyl and substituent force fields. The initial force fields are used to calculate and assign the vibrational spectra. These force fields are then refined to minimize the difference between the observed and calculated frequencies. The refined force constants are used to calculate and assign the spectra of the di- and trisubstituted benzenes.

The construction of the force fields for phenol, benzaldehyde and anisole from the benzene force fields developed in Development of a Modified Valence Force Field for Benzene section, are discussed in this section. The literature review contains a brief overview of the assignment of the phenyl modes in monosubstituted benzenes, of previous assignments of the spectra of phenol, benzaldehyde and anisole, and a more detailed discussion of prior normal coordinate analyses of these compounds. The vibrational spectra of the monosubstituted benzenes are presented. The parameters used to calculate the kinetic energy matrices and the three different approximations of the potential energy matrices are presented in a discussion of the vibrational analyses. The final force fields are evaluated and the assignments based on the potential energy distributions

calculated using these force fields are discussed. A comparison of the frequencies and intensities of the fundamental phenyl modes of the monosubstituted benzenes is presented.

LITERATURE REVIEW

The assignment of the phenyl modes in monosubstituted benzenes and previous assignments of the vibrational spectra of phenol, benzaldehyde and anisole are briefly reviewed in this section. Prior normal coordinate analyses of these compounds are also discussed in this section. Knowledge of these assignments and analyses will help to interpret the fundamental modes of the monosubstituted model compounds and aid in the evaluation of the assignments made in this investigation. The details of previous assignments of the IR and Raman spectra of phenol, benzaldehyde and anisole are presented in the discussion of the assignments proposed in this investigation.

VIBRATIONAL SPECTRA OF MONOSUBSTITUTED BENZENES

Monosubstitution of the aromatic ring lowers the symmetry of the compound. Monatomic and linear substituents result in C_{2v} symmetry. Monosubstituted benzenes with substituents having a plane of symmetry coincident with the plane of the ring have C_S symmetry though they are often described in terms of C_{2v} symmetry. Under the C_{2v} point group the thirty phenyl fundamentals are distributed as: $11a_1 + 10b_1 + 3a_2 + 6b_2$ (sometimes seen as $11a_1 + 10b_2 + 3a_2 + 6b_1$ due to a different definition of the molecular axes). The fundamental modes of the phenyl ring react in one of two ways to substitution on the aromatic ring. Either the vibration is removed from the point of substitution and is therefore relatively unchanged in frequency, or the vibration is centered about the point

of substitution and the frequency is shifted significantly. Substitution on the aromatic ring will split the degenerate modes. Of the two bands resulting from a doubly degenerate benzene mode, one will generally be fairly specific in frequency and form to the benzene vibration. The position of the other band will depend on the nature of the substitution. To some degree, the reaction of the phenyl modes to substitution can be predicted based on the number and position of the substituents. Of the thirty phenyl fundamentals, twenty-four have been found to be essentially independent of the substituent attached to the ring. In these modes the carbon atom linking the benzene ring to the substituent and the atoms of the substituent undergo insignificant displacements during the vibration. The remaining six vibrations are modes in which the substituent moves with appreciable amplitude, commonly referred to as "x-sensitive" modes. In addition to these thirty phenyl fundamentals, the internal vibrations of the substituent itself will be found in the Raman and IR spectra, three per each additional atom (e.g., there are three substituent modes in phenol, six in benzaldehyde, etc.).

The behavior of the phenyl modes on monosubstitution of the benzene ring has been reviewed by Varsanyi (6), Whiffen (21), Dollish (22) and Katritzky (23). The conclusions of these reviews as they pertain to the monosubstituted benzenes under investigation will be discussed briefly at this point. The fundamental phenyl modes of monosubstituted benzenes are discussed in full in Appendix II. Wilson's notation for benzene normal modes (Fig. 2) is used to describe the fundamentals of the phenyl group of the monosubstituted benzenes. The assignment of the phenyl modes based on these reviews is presented in Table VI.

TABLE VI

FREQUENCY RANGES FOR MONOSUBSTITUTED BENZENES

	Wavenumber, cm^{-1}
CH stretching modes	
2, 7a, 7b, 20a, 20b	2950-3120
CC stretching modes	
8a	1599-1611
8b	1582-1585
14	1300-1350
19a	1470-1515
19b	1440-1470
CH in-plane bending modes	
3	1253-1331
9a	1170-1181
15	1150-1160
18a	1027-1032
18b	1065-1082
In-plane ring deformations	
1 l; h[a]	1060-1100; 620-830
6a l; h	650-710; 300-530
6b	605-630
12	990-1010
CH out-of-plane bending modes	
5	970-1000
10a	824-847
11	728-797
17a	952-975
17b	882-938
Out-of-plane ring deformations	
4	680-700
16a	390-420
16b	430-560
CX modes	
9b CX in-plane bend	200-410
13 CX stretch	1100-1280
10b CX out-of-plane bend	140-250

[a]Light (l), < 25 amu; heavy (h), > 25 amu.

Based on the information available about monosubstituted benzenes in general, six of the thirty phenyl modes of phenol, benzaldehyde, and anisole would be expected to be substituent sensitive. On monosubstitution, one of the hydrogens of benzene is replaced by a substituent. The three modes associated with this bond are x-sensitive. The CX stretching vibration, mode 13, should arise between 1100 and 1280 cm^{-1}. The CX in-plane bend, vibration 9b, is expected to occur in the 200-400 cm^{-1} range. And the CX out-of-plane bend, mode 17b, is shifted to the 140-250 cm^{-1} range.

Two other x-sensitive modes are the in-plane ring deformations, modes 1 and 6a. The frequency ranges for these x-sensitive in-plane ring deformations are influenced by the mass of the substituent. For a light substituent (<25 amu), such as a hydroxyl group, mode 1 should arise between 620 and 830 cm^{-1}, and mode 6a should occur between 300 and 530 cm^{-1}. For heavy substituents (>25 amu), such as methoxyl and formyl groups, mode 1 is expected to occur between 1060 and 1100 cm^{-1}, and mode 6a should be between 650 and 710 cm^{-1}.

Varsanyi (6) considers the sixth x-sensitive mode to be mode 3, a CH in-plane bending mode. Whiffen (21) classifies mode 3 as X-insensitive, and identifies the sixth x-sensitive band to be an out-of-plane ring deformation, mode 16b. The frequency range for mode 3 is 1253-1331 cm^{-1}. That for mode 16b is 430-560 cm^{-1}.

The remaining twenty-four phenyl modes are substituent insensitive. These include five CH stretching, five CC stretching, five (four) CH in-plane bending, two in-plane deformation, five out-of-plane bending and two (three) out-of-plane ring deformation modes (these numbers reflect Whiffen's classifications, the

numbers in parentheses refer to Varsanyi's designations where they differ). The frequency ranges for these modes are presented in Table VI.

VIBRATIONAL SPECTRA OF MODEL COMPOUNDS

Phenol

Both theory (24) and experiment (25) have shown phenol to have a planar structure. The molecule therefore has C_s symmetry. Under this point group, the thirty-three fundamental modes divide into twenty-three A' or in-plane modes, and ten A" or out-of-plane modes. All thirty-three modes are both IR and Raman active. The IR and Raman spectra of phenol have been reported in the literature. The interpretations of these spectra have been based on group frequency information, isotopic substitution studies, Raman depolarization ratios, vapor band envelopes of the IR spectra, and simple normal coordinate treatments. Thirty of the fundamental modes originate in the aromatic ring, the remaining three arise in the hydroxyl group.

Evans (26) initially assigned the vibrational spectra of phenol by comparison to the assignments of other monosubstituted benzenes. Subsequent assignments of the IR and Raman spectra of phenol by Green (27,28), Pinchas (29), Wilson (30) and Bist (31), Kovner (32), Brand (33), and Bogatyreva (34) suggest different interpretations for several of the bands. The substituent insensitive phenyl modes, modes 14 and 3, and the six substituent sensitive phenyl modes all have a variety of assignments. The assignments of the three fundamental modes of the hydroxyl group have been well established.

Benzaldehyde

Benzaldehyde is planar (24,35). Its only element of symmetry is the reflection plane coincident with the plane of the aromatic ring, so benzaldehyde

belongs to the C_s point group. Under this point group the thirty-six fundamental modes of benzaldehyde divide into twenty-five A' (in-plane) and eleven A" (out-of-plane) modes. Theoretically, all of these fundamental modes are both IR and Raman active. The vibrational spectra of benzaldehyde have been the focus of several studies. The spectra have been interpreted using group frequency information, deuteration studies, Raman depolarization ratios, and simple normal coordinate analyses. The majority of the thirty vibrations arising from the aromatic nucleus, and of the six formyl group vibrations have been assigned.

Twenty-four of the thirty vibrations of the phenyl group are commonly thought to be insensitive to monosubstitution. The bands corresponding to these vibrations are readily interpreted by comparison to the spectra of other monosubstituted benzenes, and are generally made without comment. Garrigou-Lagrange, et al., (36), Zwarich, et al., (37), Green and Harrison (38), Puranik and Rao (39), Brown (40), Silver and Wood (41) and Lebas (42) assign all or some of the phenyl modes of benzaldehyde. On comparison of these proposed assignments, phenyl modes 19a, 19b, 18a, 18b, 14, 3, 6a, 9b and 10b are seen to have a variety of assignments. In addition to the aforementioned authors, Rao, et al., (43), Saier, et al., (44), Eggers and Lingren (45), Pinchas (46) and Miller (47) discuss the assignment of the fundamental modes of the formyl group. Of the normal modes of the formyl group, only the assignments of the in-plane aldehyde CH stretch and the out-of-plane wag of the aldehyde wag vary.

Anisole

Anisole is thought to exist in two stable conformations (48,49). In one, the heavy atoms of the methoxyl group are not in the plane of the aromatic ring.

The other has a reflection plane coincident with the plane of the aromatic ring. At room temperature anisole exists predominantly as the planar conformer (48,49).

The planar conformer of anisole has C_s symmetry. Its forty-two fundamental vibrations divide into twenty-eight A' (in-plane) and fourteen A" (out-of-plane) modes. These vibrations are all both IR and Raman active. Literature discussions of the vibrational spectra of anisole include analyses using group frequency information, deuteration studies, Raman depolarization ratios, and normal coordinate calculations.

As in phenol and benzaldehyde, thirty of the forty-two fundamental modes arise in the aromatic nucleus. Twenty-four of these thirty phenyl modes are substituent insensitive, and six are substituent sensitive modes. The methoxyl group generates the remaining twelve anisole fundamentals.

The vibrational spectra of anisole have been interpreted to some extent by Owen and Hester (50), Green (51), Stephenson, et al., (52), Briggs, et al., (53), Bogatyreva, et al.,(54), Katritzky and Coats (55), Tylli and Konschin (56) and Campagnaro and Woods (57). The proposed assignments of the fundamental phenyl modes of anisole agree except for those of modes 1, 12, 16b, 17b, 11, 10b and 9b. The assignments of several of the methoxyl modes also vary. The assignments of the antisymmetric CH stretching modes, the O-CH_3 stretch, the symmetric deformation of the CH_3 group, the rocking motions of the OCH_3 group and the in-plane COC bend vary.

NORMAL COORDINATE ANALYSES

Phenol

Kovner (32), Brand (33), and Bogatyreva (34) have used normal coordinate calculations to aid in their assignments of the vibrational spectra of phenol.

Kovner calculated both the in-plane and out-of-plane frequencies. Brand was only interested in the out-of-plane frequencies and Bogatyreva solved just the in-plane problem.

Kovner, et al., (32) calculated the vibrational spectra of phenol and deuteriophenol. The geometry and experimental frequencies were taken from Evans' (26) discussion of the vibrational spectra of phenol. The torsional vibration was not included. Initial force constants for the phenyl group were taken from similar calculations for toluene. The force constants of the hydroxyl group were originally taken to be equal to the corresponding constants for methanol. The hydroxyl force constants were later varied "using a calculation of the derivatives of certain frequencies with respect to the force constants" (32). Using the final force field the planar vibrations of phenol were calculated with an average error of 11 cm^{-1}, and the nonplanar vibrations were calculated with an average error of 9 cm^{-1}. Kovner concluded that this calculation confirmed Evans' spectral interpretation. Green (28) asserts that two erroneous frequencies were used in this work. Kovner used frequencies of 1370 and 1292 cm^{-1} for the bands associated with the COH in-plane bend rather than 1344 and 1180 cm^{-1} as accepted elsewhere. The COH in-plane bend was assigned to the band at 1370 cm^{-1}. Bogatyreva (34) also regards Kovner's use of the 1370 cm^{-1} band for the COH deformation to be in error. He disputes the assignment of the COD deformation to 990 cm^{-1} as well.

Bogatyreva (34) carried out calculations of the vibrational spectra of phenol and two of its isotopic modifications (^{18}O-phenol and ^{2}H-phenol) to attain a more accurate interpretation of the spectra of phenol. Based on a planar

structure for phenol, Bogatyreva calculated the frequencies of the planar vibrations. Force constants developed by Bogatyreva for benzene and other monosubstituted benzenes were used as the basis for these calculations. The force constants associated with the CC bonds were "lowered relative to their value in benzene due to the lowering of the electron density of these bonds in phenol." The force constants of the benzene ring related to the interaction of the ring and the substituent group, and the four force constants associated with the hydroxyl group were varied. The observed vibrational frequencies were satisfactorily calculated with an average error of 10 cm^{-1}. It was found that the COH angle bend contributes to several vibrations. To separate the frequency due principally to this deformation, Bogatyreva calculated the vibrational frequencies for a model of phenol with the C-OH bond perpendicular to the plane of the ring. In this calculation the planar COH angle deformation contributed to just the band at 1180 cm^{-1}.

Brand, et al., (33) calculated the out-of-plane vibrational frequencies of phenol to discern the extent of coupling between the OH torsion and the phenyl modes. Brand used the structure proposed by Forest and Dailey (58) for phenol, delta internal coordinates, and the observed frequencies given in an earlier paper (31) for these calculations. The force field consisted of twenty-two independent force constants. The refined force field calculated the observed frequencies with an average error of 5.5 cm^{-1}. The substituent was found to mainly influence the force constants associated with the bonds adjacent to the hydroxyl group. The constants for the lower portion of the ring were virtually unchanged from those in benzene. The OH torsion was found to couple only slightly with the other out-of-plane vibrational modes of phenol.

Benzaldehyde

Puranik and Rao (39) and Zwarich, Smolarek and Goodman (37) have used normal coordinate calculations to aid in their interpretation of the vibrational spectra of benzaldehyde. Puranik and Rao investigated compounds of the type C_6H_5COX where X was CH_3, H, F or Cl, looking only at the force constants of the C-COX group. Zwarich, et al., were interested in providing a basis for analyzing the forbidden part of the $\pi^* \leftarrow n$ electronic spectrum appearing in the near UV, and used normal coordinate calculations to assign the out-of-plane modes of benzaldehyde.

Puranik and Rao (39) simplified the normal coordinate analysis of benzaldehyde by assuming the phenyl group to be a point mass, and therefore a four-body problem. The planar model belongs to the C_s point group and has five in-plane and one out-of-plane vibration. Consistent with an assumption of a point mass phenyl group, only the normal vibrations associated with the bonds linked to the phenyl group as one entity were considered. A simplified quadratic force field was used. Initial force constants were taken from related molecules and varied to get a close fit between the observed and calculated values of the fundamental frequencies. Puranik and Rao concluded that their assumption of a point mass phenyl group was justified, since the differences between the observed and calculated frequencies were within one percent.

Zwarich, et al., (37) used a more complete model for the normal coordinate analysis of benzaldehyde. The structural parameters used for the planar benzaldehyde molecule were a composite of those of the related molecules, acetaldehyde, benzoic acid and benzene. A valence force field comprising force

constants transferred from benzene and acetaldehyde was used to calculate the frequencies of the benzaldehyde in-plane fundamentals. Minor alterations in bond stretching and angle bending force constants were made to compensate for force constant variations with geometry, but no attempt at refinement was made. This force field calculated the observed frequencies of benzaldehyde with an average error of 16 cm^{-1} over the twenty-five in-plane frequencies calculated.

Zwarich treated the out-of-plane calculation basically as a benzene problem (37). The internal coordinate definitions of the out-of-plane hydrogen wags and torsions and the force constants given by Whiffen (8) were used for the phenyl group. The internal coordinate associated with the out-of-plane wag of the formyl carbon with respect to the benzene ring was taken to be analogous to an out-of-plane hydrogen wag and given the same force constant and interaction constant values. The torsional barrier of the formyl group against the phenyl group was assumed to be small, so the interaction force constants associated with this internal coordinate were not included in the calculation. This out-of-plane force field calculated the observed frequencies of benzaldehyde with an average error of 14 cm^{-1} over the eleven out-of-plane frequencies calculated.

Anisole

Two separate normal coordinate analyses have been carried out for anisole. Talberg (59) calculated the frequencies of anisole and nitrosobenzene in order to get a reliable assignment for the p-nitrosoanisole modes. Bogatyreva, Kotov, and Shishkina (54) performed their normal coordinate analysis of anisole to interpret its vibrational spectra.

Talberg assumed a ring geometry of a regular hexagon and used Seip's (48) proposed bond lengths and angles for the methoxyl group. Nonplanar vibrations of the ring and the COC group, and the torsional vibrations were not considered. The thirteen parameter model valence force field developed by Duinker and Mills (14) for benzene, was used for the phenyl portion of the force field. The OCH_3 portion of the force field was one "generally used at this institute" (University of Oslo) (59). The observed frequencies of Bogatyreva (54) were used. Except for modes 6a and 6b, Bogatyreva's assignments were used. Talberg's force field calculated the observed frequencies of anisole with an average error of 22.4 cm^{-1}.

Bogatyreva, et al., (54) used a geometrical model of anisole in which the plane of the benzene ring and the COC group form a 22° angle. A COC angle of 110° was used. The remaining structural parameters were taken from the work of Goodwin, et al., (60). The nonplanar vibrations of the ring and the COC group and the torsional vibrations of the methoxyl group were not included in the calculations. The initial force field was based on force fields developed for benzene and toluene and for methanol (54). The final set of force constants for the ring was obtained by solving "the inverse spectrum problem" (54). Force constants associated with the CCH angle bends fluctuated more than other constants. The final force field calculated the observed frequencies with an average error of 13.5 cm^{-1} over the thirty-one frequencies considered. To confirm their assignments, the calculation was repeated using a point mass of mass 15 to represent the CH_3 group.

EXPERIMENTAL

SAMPLES

Samples of benzaldehyde and phenol were available from other research efforts at IPC. Benzaldehyde and phenol had been purchased from Mallinckrodt, Inc. Anisole was purchased from Aldrich Chemical Company, Inc. All were used without further purification. These compounds were characterized by comparison to their infrared spectra published by Sadtler (61) in the range 400-4000 cm^{-1}. They were also compared to other published spectra.

MEASUREMENT OF SPECTRA

Infrared spectra of phenol, benzaldehyde and anisole were recorded for the pure liquid samples and for carbon tetrachloride and carbon disulfide solutions of these compounds. The liquid spectra were recorded with the sample between NaCl windows. The solution spectra were recorded in a 0.0225 mm fixed NaCl cell. These spectra were recorded using a Nicolet FT-IR 7199c spectrophotometer over the range 400-4000 cm^{-1}.

The Raman spectra of the monosubstituted benzene derivatives were recorded for the pure liquid samples, and for solutions of these compounds. Carbon tetrachloride and water were used as solvents for phenol. Carbon tetrachloride and methanol were used as solvents for anisole and benzaldehyde. The spectra were measured with the liquid or solution in a capillary tube. The scattered radiation was observed 90° from the incident beam. Unpolarized, and both parallel and perpendicularly polarized spectra were recorded from 50 to 3800 cm^{-1}. These spectra were obtained using a Jobin Yvon Ramanor HGS2 spectrometer.

The 514.5 nm line of an argon ion laser was used as the radiation source. The instrumental parameters are listed in Table VII.

TABLE VII

EXPERIMENTAL PARAMETERS FOR IR AND RAMAN SPECTRA

Infrared

Instrument: Nicolet FT-IR Spectrophotometer, Model 7199c

Control Settings:
Resolution: 2 cm^{-1}
No. Scans: 100

Raman

Instrument: Jobin Yvon Ramanor HGS2 Spectrometer

Control Settings:
Scan Speed: 1000 ms/channel
No. Scans: 4
Resolution: ca. 3 cm^{-1} (slit width of 150 um)

Laser: Coherent Radiation Argon Laser, Model 52a
Wavelength: 514.5 nm
Power: 0.3-0.5 watt

EXPERIMENTAL RESULTS

The vibrational spectra of the monosubstituted benzene derivatives are reproduced in Fig. 4-6. The corresponding band positions are tabulated in Tables VIII-X. The IR and Raman solution spectra of the monosubstituted benzenes are included in Appendix III. The main features of the spectra recorded for the dilute solutions of these compounds are very similar to those of the spectra of the pure compounds. The principal differences appear to be due to a change in the hydrogen bonding of the sample.

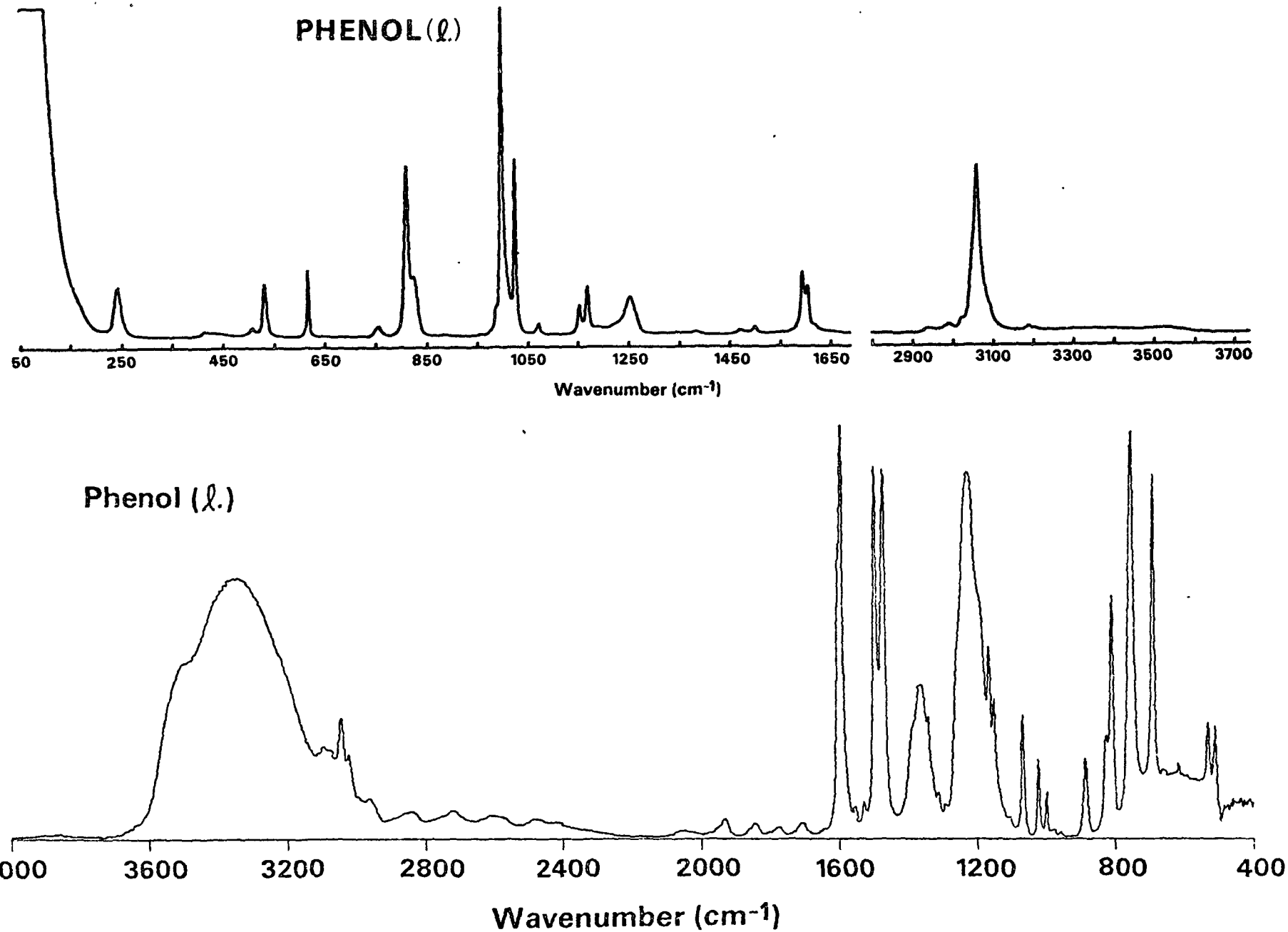


Figure 4. Raman (upper) and infrared (lower) spectra of phenol.

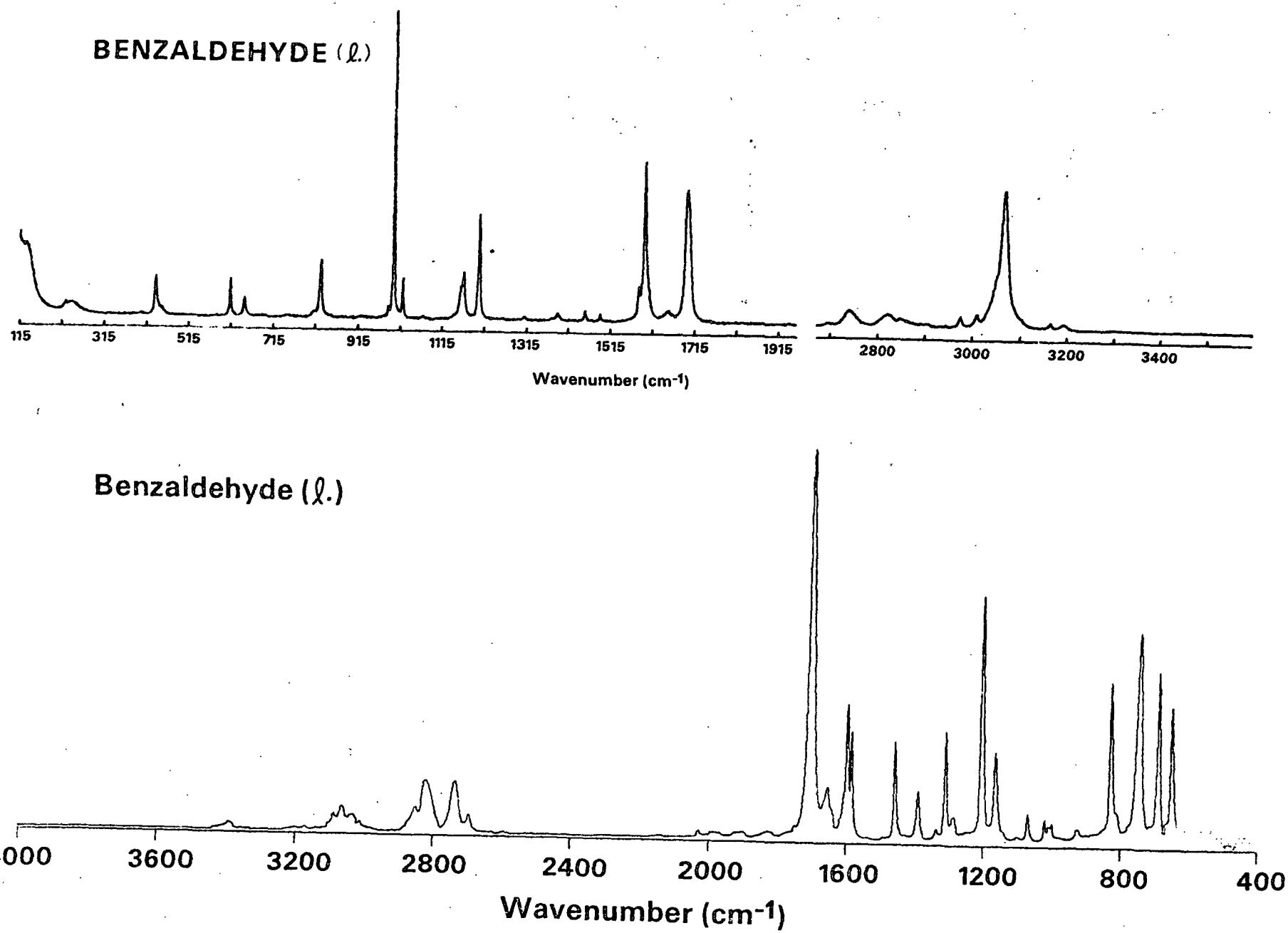


Figure 5. Raman (upper) and infrared (lower) spectra of benzaldehyde.

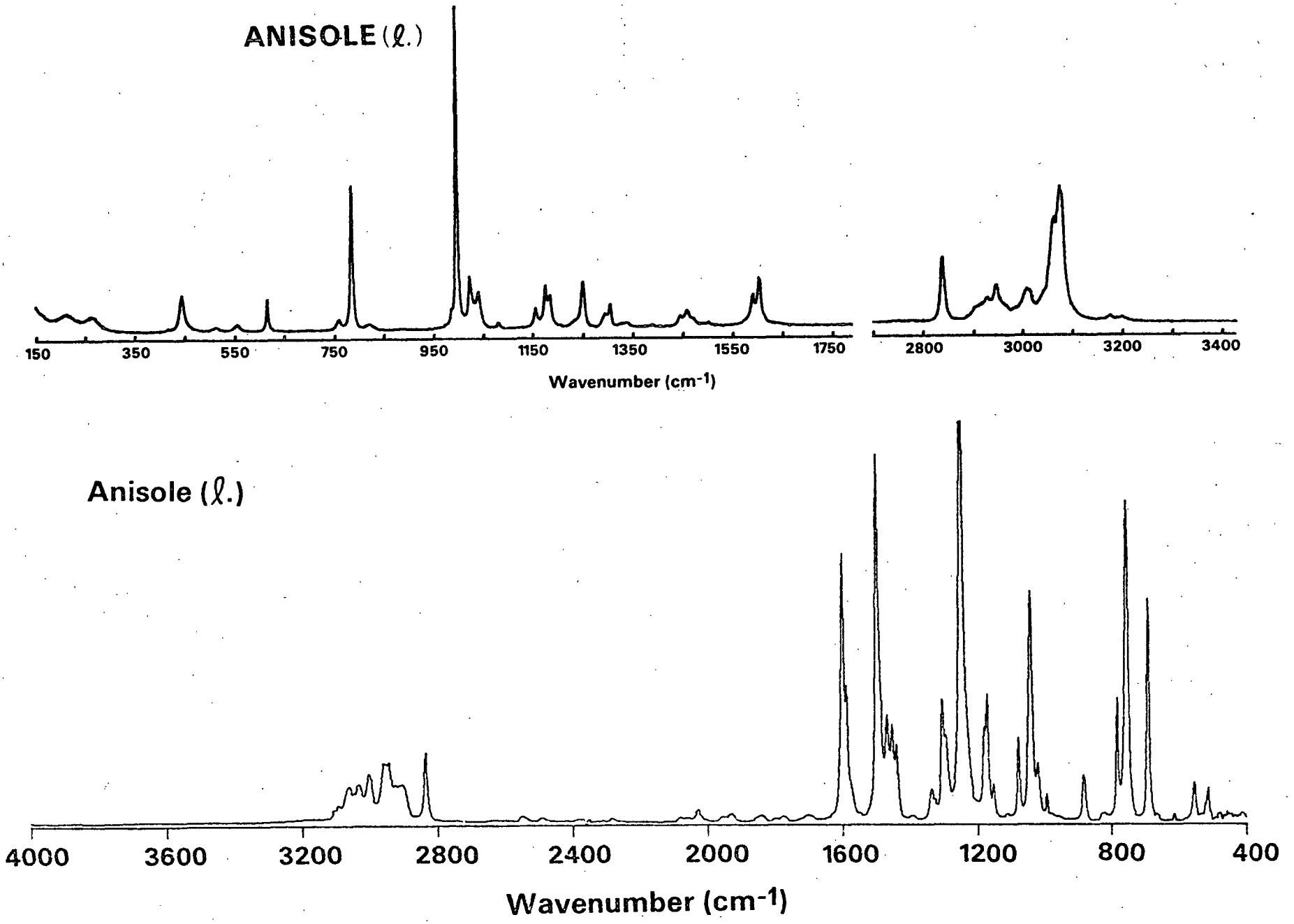


Figure 6. Raman (upper) and infrared (lower) spectra of anisole.

TABLE VIII

SPECTRAL DATA - PHENOL (LIQUID)

Infrared, cm^{-1}	Raman, cm^{-1}
	242 m[a]
	416 w
511 m	509 w
533 m	531 m
618 w	618 m
661 w	
691 vs	690 vw
753 vs	756 w
810 s	812 s
826 m	826 m
887 m	890 vw
959 vw	958 vw
978 vw	986 m
1000 vw	1001 vs
1024 m	1026 s
1071 m	1073 w
1108 vw	
1153 m	1154 m
1169 s	1170 m
1180 sh	1192 w
1228 vs	1220 sh
	1252 m
1291 w	
1315 m	
1345 m	
1365 m	
1389 sh	1380 w
1473 vs	1470 w
1499 vs	1500 w
1529 w	
1557 w	
1596 vs	1594 m
1604 sh	1606 m
	1622 w
3024 m	3022 w
3046 m	
3076 m	3061 s
3093 m	
3108 m	
3340 s	
3348 s	3512 w

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

TABLE IX

SPECTRAL DATA - BENZALDEHYDE (LIQUID)

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	128 m[a]	2696 w	2693 w
	223 w	2737 m	2737 m
	237 w	2820 m	2819 m
410 w		2850 m	2847 w
435 w	438 m	3012 w	3007 w
448 w	451 w	3031 w	
506 w			3046 sh
523 mw		3064 m	3063 m
533 mw		3086 w	
615 mw	614 m		3101 w
650 s	649 m		3163 w
665 w			3190 w
689 s		3390 w	
746 s	746 w		
813 sh	811 w		
828 s	827 m		
924 w	851 w		
	987 w		
1001 m	1000 vs		
1008 w			
1023 m	1022 m		
1072 m	1072 w		
1101 w			
	1147 sh		
	1160 sh		
1167 ms	1166 m		
1204 s	1202 s		
1265 vw			
1288 m			
1311 ms	1311 w		
1339 w			
	1377 sh		
1391 m	1390 w		
1429 vw			
1456 ms	1455 w		
	1490 w		
1584 ms	1584 sh		
1597 s	1596 s		
1654 ms	1652 w		
1703 vs	1696 s		

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

TABLE X

SPECTRAL DATA - ANISOLE (LIQUID)

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	214 m[a]	2836 m	2836 s
	266 m	2905 w	2906 w
414 vw	416 vw	2924 w	2924 m
459 vw	443 s	2945 m	2945 m
478 vw		2957 m	2956 w
514 w	513 w	3003 m	3004 m
554 w	553 w	3033 w	3037 sh
614 vw	614 s	3063 w	3055 s
667 vw		3093 w	3069 s
692 s	695 vw		
756 s	757 w		
784 m	784 vs		
820 vw	820 w		
884 m	885 vw		
	942 vw		
960 vw	975 m		
	988 vw		
995 w	995 vvs		
1021 m	1021 s		
1041 s	1039 s		
1078 m	1078 w		
1110 vw	1112 vw		
1153 w	1153 m		
1173 m	1172 s		
1181 m	1181 s		
	1228 vw		
1249 vs	1247 s		
1293 m	1291 m		
1303 m	1302 m		
	1325 w		
1336 w	1336 w		
1394 vw	1383 vw		
1442 m	1441 m		
1454 m	1455 m		
1468 m	1468 w		
1498 s	1497 w		
	1548 w		
1588 m	1587 s		
1601 s	1600 s		

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

VIBRATIONAL ANALYSIS

As discussed in Appendix I, a normal coordinate analysis requires specification of the kinetic and potential energy matrices. The eigenvalues of the product of these matrices are related to the normal frequencies of vibration. The corresponding eigenvectors are the normal modes of vibration of the system. The calculation of the kinetic and potential energy matrices, and the solution of the secular equation for the normal frequencies and modes are presented in this section.

KINETIC ENERGY MATRIX

The kinetic energy matrix, or G matrix is constructed from information about the atomic masses, molecular bond lengths and bond angles, and the internal coordinates to be used in the problem.

Geometry

Phenol, benzaldehyde, and anisole are theoretically predicted to have, and have been experimentally shown to have, stable planar structures. The bond lengths and angles for phenol, benzaldehyde and anisole are assumed from the experimentally determined structures of similar molecules.

Based on molecular orbital calculations, Hehre, et al., (24) predicted planar conformations for the monosubstituted benzene derivatives. Conjugation effects between the ring and the substituent cause partial double bond character of the C-X bond. This results in stable planar conformations for these molecules. Anisole is predicted to have two stable conformations: the planar structure and one in which there is a small rotation out-of-plane about the C-O bond. This second structure results from steric interaction between the methoxyl group and

the (cis) ortho hydrogen in the planar conformer. The planar conformation is predicted to be slightly more stable.

The structures adopted for the model compounds are composites of the structures of related molecules. For all three compounds the phenyl ring is assumed to have the dimensions of the benzene ring (1). The structural parameters of the hydroxyl group are those used by Evans (26). The parameters of the formyl group of benzaldehyde are the compromise between the structures of acetaldehyde (62) and benzoic acid (63) enlisted by Zwarich, et al., (37). The structure of the methoxyl group derived from that of solid 1,4-dimethoxybenzene (64) by Tylli (56) is used for anisole.

Experimental determinations of the structure of phenol and benzaldehyde were not found in the literature. The structure of gaseous anisole has been determined from electron diffraction data (48). However, this structure is not used in this study. The structure is to be used to determine force constants for liquid anisole, to be transferred to the force field for vanillin, a solid at room temperature. For this reason it was thought that the structure derived from that of solid 1,4-dimethoxybenzene would be better. There are two principal differences between this structure for anisole and that calculated by Seip (48). One is the length of the $O-CH_3$ bond. Seip found it to be 1.423 Å. Tylli (56) used a value of 1.35 Å for this bond length. The other difference is the CCO angles. Seip found one to be 116°, the other, 124°. In the model used here both are 120°. The structural parameters used in this study for the model compounds are listed in Table XI.

TABLE XI

STRUCTURAL PARAMETERS ADOPTED FOR THE MONOSUBSTITUTED BENZENES

Phenyl Group		Methoxyl Group	
C-C	1.397Å	C-O	1.36Å
C-H	1.084	O-C	1.35
CCC	120°	C-H	1.11
CCH	120°	CCO	120°
		COC	121°
Formyl Group		OCH	109.5°
C-C	1.48Å		
C=O	1.24	Hydroxyl Group	
C-H	1.084	C-O	1.360Å
CCC	120°	O-H	0.960
CCO	125°	CCO	120°
CCH	115°	COH	118°

The monosubstituted benzene derivatives have a plane of symmetry coincident with the aromatic ring. Due to this plane of symmetry the normal modes can be separated into in-plane and out-of-plane modes. Since these modes are orthogonal the vibrational problem can be separated into an in-plane and an out-of-plane problem. Phenol and benzaldehyde have all atoms in this plane, so the internal coordinates and the force constants for the in-plane and out-of-plane problems are independent, and the two problems can be set up and solved independently. Anisole has two atoms out of the plane of symmetry so the internal coordinates and force constants for the two problems are not independent. Several of the internal coordinates and force constants used to describe the in-plane problem are also used to describe the out-of-plane problem. Transformation to symmetry coordinates is needed to separate the problems for anisole. For all three molecules the elements of the in-plane and out-of-plane problems are developed separately.

Internal Coordinates

The secular equation is set up in internal coordinates. Internal coordinates use the changes in bond lengths and bond angles to describe the relative positions of the atoms in a molecule. The internal coordinates for the model compounds are a composite of those used for benzene and those defined for the substituent.

The in-plane modes of the phenyl group in all three compounds are described by a set of twenty-seven internal coordinates. These include six CC bond stretches, five CH bond stretches, ten CCH angle bends and six CCC angle bends. The three internal coordinates associated with the CX bond (the CX stretch and the two CCX angle bends) are also similarly defined in all three compounds. In addition to this basic set of thirty internal coordinates (analogous to the thirty defined for benzene), coordinates are added to describe the vibrations of the substituent.

Two additional coordinates are defined for phenol: the OH stretch and the COH angle bend. Benzaldehyde has five additional in-plane internal coordinates: the C=O stretch, the CH stretch, the CCO angle bend, the CCH angle bend, and the OCH angle bend. For anisole the additional internal coordinates defined are: the O-CH_3 stretch, three CH stretches, the COC angle bend, three OCH angle bends and three HCH angle bends. Three of the modes that can be described by these coordinates are A" modes. These are separated by transforming to symmetry coordinates.

The out-of-plane modes of the phenyl groups in these compounds are described by a set of eleven internal coordinates. The five CH out-of-plane wags and six torsions about the CC bonds make up this set. The torsions, as

defined in benzene, are taken to be the linear combination of the two torsions: $H_1C_1C_2C_3$ and $C_6C_1C_2H_2$. The out-of-plane wag of the CX bond is the only other internal coordinate that is similarly defined for all three model compounds. These twelve internal coordinates correspond to the set defined for benzene. In addition to this base set, the internal coordinates for phenol include the torsion about the CO bond. Description of the out-of-plane modes of benzaldehyde requires the definition of two out-of-plane wags (CO and CH) and the torsion about the CC bond. Two torsional coordinates complete the set for anisole: the torsion about the CO bond and that about the OC bond. As in the torsions of the phenyl ring, all torsions in these substituents are defined to be the linear combinations of the possible torsions about that bond.

Each of these sets of internal coordinates includes redundancies. A forty-five member set of internal coordinates is defined for phenol. This set includes twelve redundant coordinates, all of which result from the definition of the internal coordinates of the ring. The set of fifty internal coordinates defined for benzaldehyde includes fourteen redundant coordinates. Twelve of these, again, are due to the definition of the coordinates of the ring and two arise from the substituent coordinates (one of the in-plane angle bends and one out-of-plane wag are redundant). The set of internal coordinates defined for anisole has fifty-five internal coordinates, thirteen of which are redundant. These redundant coordinates include one of the set of six angles defining the OCH_3 group and twelve due to the definition of the ring coordinates. The internal coordinate definitions are listed in Appendix IV.

POTENTIAL ENERGY MATRIX

Given the masses of the atoms, the structure of the molecule and the force constants for the molecule, the secular equation can be solved for the normal

frequencies. Or, given the atomic masses, molecular structure, and the normal frequencies, the force constants (in a simplified force field) can be calculated. In most calculations, however, neither the force constants nor all the normal frequencies are known. In this situation an approximate force field is used to calculate the frequencies. This calculation aids in the assignment of the vibrational spectrum. The analysis either stops at this stage, or this spectral assignment is then used to refine the force constants. The force constants are refined to improve the force field by minimizing the difference between the observed and calculated frequencies. The refinement may indicate that changes are needed in either the assignment or in the force field. So, the refinement process may need to be repeated several times before a satisfactory force field is developed. Refinements of initial force fields are usually carried out to develop force constants transferable to a different system. Such is the case in this investigation. The force fields developed for the monosubstituted benzene derivatives are to be used to calculate the frequencies and assign the spectra of the di- and trisubstituted benzene derivatives.

Neither the force constants nor all the normal frequencies are known for the monosubstituted model compounds. Therefore it is necessary to assume an initial force field. In this assumption both the form of the force field and the initial values of the force constants must be specified. Two different types of force field and one structural approximation are used in these calculations. The two force fields used are a zeroth approximation force field and a modified valence force field. The structural approximation is the point mass approximation.

Point Mass Approximation

The point mass approximation assumes a portion of the molecule to have all its mass concentrated at a point. In this calculation the substituent groups were considered to be point masses. Masses of 17, 29, and 31 were used to represent the hydroxyl, formyl and methoxyl groups, respectively. Benzene geometry and internal coordinates were used to set up the G matrix for these point mass substituted benzenes. The twenty-two parameter benzene force field [based on Painter's force field (13)] was used without alteration. Calculations using point masses of 2, 4, and 8 were also performed. The results of these calculations are shown in Table XII and Fig. 7.

Though the point mass approximtion is an oversimplification of the problem, these calculations do demonstrate the effect monosubstitution of the ring and the mass of the substituent have on the frequencies of the fundamental ring modes. The results of these calculations indicate that on monosubstitution the frequencies of the majority of the modes shift at least slightly. Increasing the mass of the substituent from 2 to 31 has little effect on most of the frequencies. For example, the frequencies for the "methoxyl" compound (mass of 31) were found to be within 15 cm-1 of those for a compound with a substituent of mass 2. However, ten of the modes are substantially influenced by the mass of the substituent: 13, 8a, 19a, 1, 6a, 18b, 6b, 10b, 11 and 16b. In the literature, benzene modes 1, 6a, 3(16b), 13, 9b, and 10b are labeled substituent sensitive modes. The differences in these listings are most likely due to a difference in the definition of the sensitivity level. The neglect of the electronic effects of the substituent, the change in length of the CX bond, and the change of the force constants associated with this bond may also have an effect on the results.

TABLE XII

EFFECT OF THE MASS OF THE SUBSTITUENT ON THE CALCULATED WAVENUMBERS (CM^{-1}) OF THE MODES OF POINT-MASS SUBSTITUTED BENZENE

Symmetry Species	Mode	1	2	4	8	17	29	31
A_1	2	3063.9	3061.7	3061.7	3061.7	3061.7	3061.7	3061.7
	20a	3055.1	3049.2	3049.2	3049.1	3049.1	3049.1	3049.1
	7a	3042.9	3038.4	3038.4	3038.4	3038.4	3038.4	3038.4
	13a	3036.7	2283.5	1836.4	1686.2	1653.0	1645.6	1645.1
	8a*	1594.1	1584.7	1559.8	1529.1	1516.8	1513.6	1513.3
	19a*	1482.6	1474.2	1442.5	1353.7	1277.8	1252.8	1250.6
	9a	1178.6	1177.7	1176.2	1173.6	1170.1	1167.8	1167.5
	18a	1038.8	1034.8	1032.2	1030.9	1030.3	1030.0	1030.0
	12	1012.5	1006.9	1004.2	1003.3	1002.9	1002.8	1002.8
	1*	994.4	980.3	935.2	853.7	771.3	739.2	736.4
	6a*	608.2	601.6	586.8	553.5	483.3	421.9	414.4
B_1	20b	3055.1	3055.1	3055.1	3055.1	3055.0	3055.0	3055.0
	7b	3042.9	3042.9	3042.9	3042.9	3042.8	3042.8	3042.8
	8b	1594.1	1594.1	1594.1	1594.1	1594.5	1594.8	1594.5
	19b	1482.6	1455.9	1450.9	1449.2	1445.4	1444.5	1445.2
	3	1348.1	1327.3	1324.8	1324.1	1323.7	1323.7	1323.6
	14	1308.8	1297.6	1293.8	1292.4	1287.5	1286.3	1287.3
	9b	1178.6	1158.8	1158.3	1158.2	1157.8	1157.7	1157.7
	15	1149.0	1083.9	1076.6	1074.7	1072.3	1071.7	1072.1
	18b*	1038.8	859.1	685.7	639.8	633.0	632.6	631.6
	6b*	608.2	600.9	564.5	464.2	308.9	258.7	270.8
A_2	17a	968.3	968.3	968.3	968.3	968.3	968.3	968.3
	10a	849.5	849.5	849.5	849.5	849.5	849.5	849.5
	16a	404.5	404.5	404.5	404.5	404.5	404.5	404.5
B_2	5	990.1	983.7	983.4	983.3	983.3	983.3	983.3
	17b	968.3	924.9	917.1	914.7	911.8	911.2	911.6
	10b*	849.5	779.0	756.5	749.8	740.6	738.6	740.0
	4	704.2	699.0	697.4	696.9	697.8	698.1	697.7
	11*	672.3	606.7	536.9	504.1	471.2	464.3	468.3
	16b*	404.5	383.0	342.0	293.1	223.0	198.3	204.9

*Substituent sensitive modes.

Zeroth Approximation Force Field

A zeroth approximation force field results from merging the force fields for the individual components of a molecule without changing the values of the force constants and without introducing any new interaction force constants

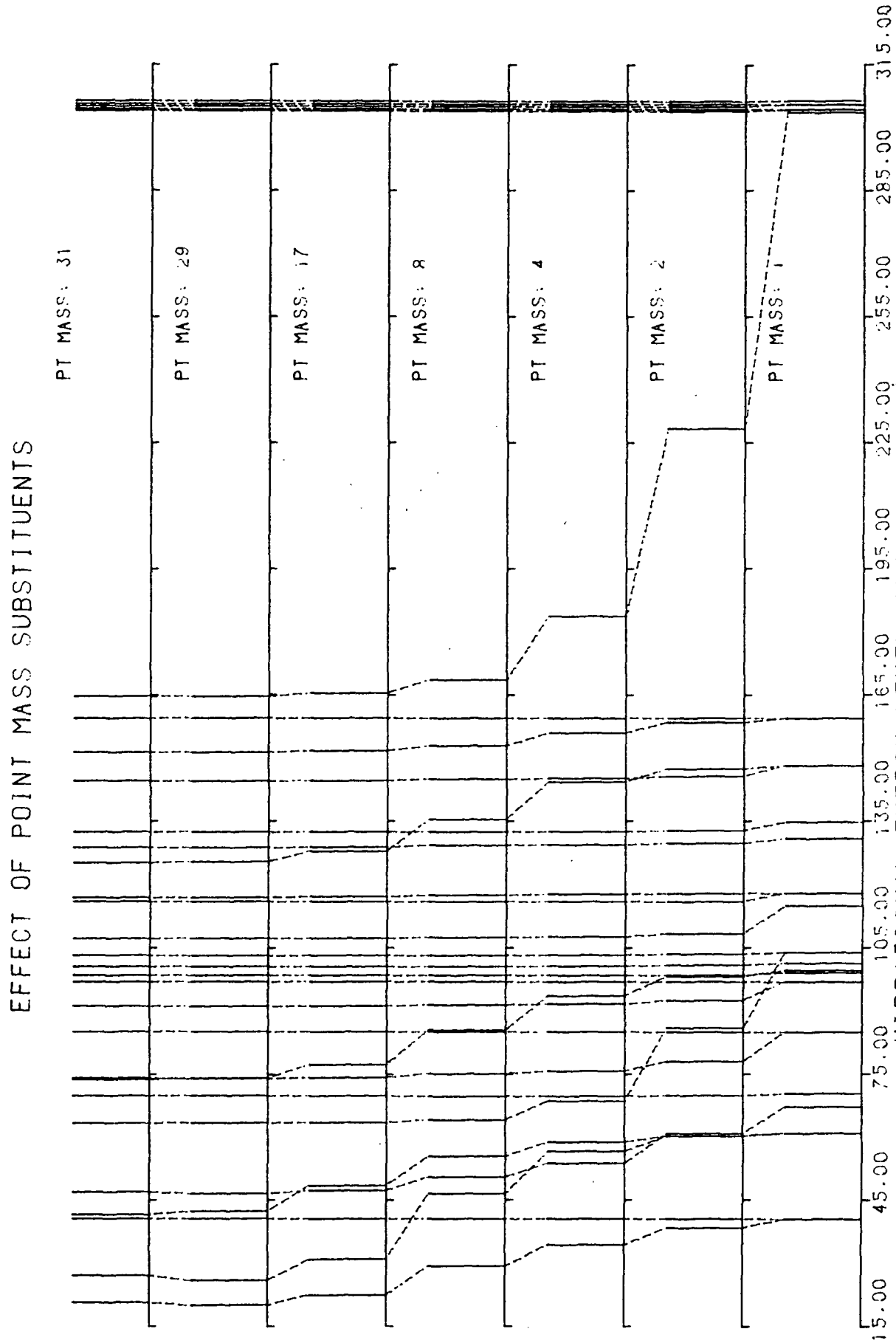


Figure 7. Effect of the mass of the substituent on the frequencies of mono-substituted benzenes.

(65). For the monosubstituted benzene derivatives this force field is constructed by adding the force field for the substituent, taken from a simple compound, to the benzene force field.

Phenol

The zeroth approximation force fields for the in-plane modes of phenol comprised the benzene force fields described in Chapter I and a hydroxyl force field transferred from methanol. Both the eleven parameter benzene force field [developed from Neto's benzene force field (15)] and the twenty-two parameter benzene force field were used. These fields were unaltered except for the replacement of a diagonal CH stretching force constant by that for the CO stretch. All interaction constants between the ring and this CO stretch retained their benzene values. CCH angle bending force constants, both diagonal and interaction, were used to describe the CCO angle. The hydroxyl force field was composed of the three diagonal force constants for the CO stretch, the OH stretch, and the COH band, and three interaction force constants relating these internal coordinates. Initial values for the hydroxyl force constants were taken from two different methanol force fields, one developed by Kovner (32) and one developed by Gebhardt (66).

The out-of-plane zeroth approximation force field for phenol was constructed from the benzene out-of-plane force field and two diagonal hydroxyl force constants. The benzene out-of-plane force field was used without change, except for the substitution of the diagonal force constant of the CO out-of-plane wag for that of one of the CH out-of-plane wags. All interaction constants between the ring and this wag retained their benzene values. In addition to the diagonal force constant for the CO out-of-plane wag, a diagonal force constant was

included for the COH torsion. The initial values for these hydroxyl force constants were taken from Zwarich's benzaldehyde calculations (37).

Benzaldehyde

A phenyl force field from benzene, and a formyl force field from acetaldehyde were used to construct the zeroth approximation force field for benzaldehyde. The in-plane phenyl force field was based on the eleven parameter benzene force field described in Chapter I. The only substitution in this field was the replacement of one of the CH stretching diagonal force constants by that of the CC stretch. The CCC angle bends associated with this bond and all interaction force constants between the aromatic ring and these coordinates were retained at their original benzene values. In addition to the diagonal force constant for the CC stretch, diagonal force constants were included for each of the internal coordinates associated with the formyl group. Constants were also included for the interaction between the CC and CO stretches, between the CO and CH stretches and between the CC stretch and CCH bend. The initial values for these force constants were taken from Cossee's acetaldehyde force field (67).

The out-of-plane benzene force field described in Chapter I was used for the phenyl portion of the out-of-plane force field for benzaldehyde. Substitution of the diagonal force constant for the CC out-of-plane wag for that of one of the CH out-of-plane wags was the only change in this force field. Addition of diagonal force constants for the CH and CO out-of-plane wags and for the torsion about the CC bond completed the description of the out-of-plane modes of the formyl group. The initial values for the formyl force constants were taken from Zwarich's benzaldehyde calculations (37).

Anisole

Zeroth approximation calculations for anisole were based on a force field formed from a force field for benzene and a force field for methyl ether. The eleven parameter benzene force field was used to describe the phenyl modes. Again, the only change in this force field was the substitution of the diagonal force constant of the CO stretch for that of one of the CH stretches. The force constants for the CCO angles and all interaction constants between this bond and the ring were kept at their analogous benzene values. The methoxyl force field consisted of the diagonal force constants for each of the internal coordinates of the methoxyl group, and seven interaction constants. The interaction constants were for the interactions between the CO and OC stretches, between the CO stretch and COC bend, between the OC stretch and COC bend, between the OC stretch and each of the three OCH bends, between the three CH stretches, between the three OCH bends and between the COC bend and each of the three OCH bends. The dimethyl ether force field developed by Snyder and Zerbi (68) was the source of the initial values for the methoxyl force constants.

The out-of-plane benzene force field developed in this investigation was used as the initial phenyl force field for the out-of-plane zeroth approximation force field for anisole. One of the CH out-of-plane wags was replaced by the CO out-of-plane wag as was the corresponding diagonal force constant. The remainder of the field was unaltered. Three of the out-of-plane modes of the methoxyl group are described by the methoxyl force constants listed for the in-plane force field. Diagonal force constants for the CO and OC torsions plus an interaction constant between these torsions were added to complete the out-of-plane methoxyl force field. Similar force constants from benzene and methanol force fields provided initial values for these constants.

In practice, the entire anisole force field was set up in internal coordinates and then factored into in-plane and out-of-plane force fields by a transformation to symmetry coordinates.

Results of Zeroth Approximation Calculations

Calculations using a zeroth approximation force field give a rough estimate of the fundamental frequencies of a molecule. The phenyl and substituent modes that are insensitive to substitution are fairly well approximated. Larger differences between the observed and calculated frequencies are found for the modes sensitive to substitution. Using the zeroth approximation force field, the in-plane modes of phenol, benzaldehyde and anisole are calculated with average errors of 26.48 cm^{-1} or 2.240% (using the eleven parameter force field), 16.95 cm^{-1} or 1.277%, and 19.54 cm^{-1} or 1.882%, respectively. The out-of-plane modes are calculated with average errors of 28.75 cm^{-1} or 6.103%, 16.75 cm^{-1} or 4.337%, and 23.40 cm^{-1} or 5.917%. The potential energy distributions calculated using these force fields are also fairly accurate. Zeroth approximation force fields are adequate for quick calculations.

Modified Valence Force Fields

Though better than the point mass approximation, the zeroth approximation is still crude. The influence of the substituent on the force field of the aromatic ring and the influence of the ring on the force field of the substituent are neglected. Both additional interaction force constants and refinement of this force field are needed to improve these calculations.

The strategy used in developing the modified valence force fields (MVFF) for the monosubstituted compounds is to first develop a MVFF for phenol in order to determine which interaction constants are necessary to accurately calculate

the normal frequencies of phenol and then to use this force field as a guide in setting up the MVFF's for benzaldehyde and anisole.

In-plane Force Fields

Phenol. In the zeroth approximation calculations of the in-plane modes of phenol, CCH angle bending force constants, both diagonal and interaction, were used to describe the CCO angle. As well, all interaction force constants between the CO stretch and the phenyl ring were retained at their original phenyl (CH) values. The first improvement on the zeroth approximation calculations was to refine these force constants, defining them to be independent of their benzene analogs. To further improve this field, two new interaction force constants were introduced: an interaction constant between the CO bond stretch and the adjacent CC bond stretches, and an interaction constant between the COH angle bend and the OCC angle bend. These force constants were initially given values of analogous interactions in benzene. These changes were made in both of the in-plane zeroth approximation force fields defined for phenol, the eleven parameter benzene force field, and the twenty-two parameter force field. These force fields were refined using a nonlinear refinement procedure based on the method of Fletcher-Powell (69,70). Two different refinement strategies were used. One was to refine the full field of force constants simultaneously. The other was to refine just the force constants associated with the substituent group while holding the rest constant, followed by a refinement of the phenyl force constants, constraining the substituent force constants to their refined values. The second method usually gave the best results.

Using the refined MVFF's for phenol the frequencies of the in-plane modes of phenol were accurately calculated. However, the potential energy distribution

calculated using these MVFF's was not reasonable. Dilution and deuteration studies of phenol identified two fundamentals to which the COH planar bending mode contributes. The predominant contribution of this bend is to the band at 1175 cm^{-1}, but some COH bending motion is involved in the fundamental derived from benzene mode 14 occurring at 1339 cm^{-1}. The potential energy distributions of the refined MVFF's did not show the COH bend contributing to either the 1175 cm^{-1} or the 1339 cm^{-1} bands.

Of the two MVFF's developed for phenol, that based on the eleven parameter benzene force field calculated the observed frequencies with a lower average error. Since the object of this study is to develop a force field to aid in the interpretation of the spectra of lignin model compounds, not as a unique phenol force field, it is felt that the simplest force field that successfully calculates the observed frequencies with a reasonable potential energy distribution is best. For this reason further development of force fields for the substituted benzene derivatives was restricted to force fields based on the simpler benzene force field, that developed from Neto's benzene force field (15).

A review of the literature shows that most of the force fields developed for other monosubstituted benzenes, (e.g., toluene and halobenzenes) contain interaction constants between the CCH angle bends; the initial modified valence force field did not. The next step in developing the phenol force field was to include these interaction constants. Ortho, meta and para CCH,CCH interaction force constants and the corresponding CCO,CCH interaction force constants were successively added to the field. These force fields were refined, both as a full field and in parts. Initial values of these force constants were from force fields for other monosubstituted benzene derivatives (71,72).

Merely including these CCH interaction constants did not significantly alter the calculated potential energy distributions. However, on refinement reasonable potential energy distributions were attained. The addition of the ortho CCH,CCH and the corresponding ortho CCO,CCH interaction force constants was sufficient for this change. For simplicity the meta and para CCH,CCH and CCO,CCH interaction constants were not included in the final in-plane force field for phenol.

The final phenol in-plane force field has twenty-four force constants: twelve associated with the phenyl ring and twelve associated with the hydroxyl group and the interactions between this group and the ring. The final force constants were based on a two part refinement, first refining the substituent force constants (including those for interactions between the substituent and the phenyl group) constraining the phenyl force constants to their initial values, then using these substituent force constants, refining the phenyl force constants. Using the final force field the twenty-three in-plane fundamentals were calculated with an average error of 4.95 cm^{-1} or 0.511%. Subsequent unrestrained refinement did not significantly change the results. A list of the force constants included in this force field and their initial and final values is presented in Table XIII. The observed and calculated frequencies of the normal modes and the potential energy distribution calculated using this force field are given in Table XIV.

Benzaldehyde. To develop an in-plane modified valence force field for benzaldehyde, the same strategy was followed as that used to develop the phenol force field. Force constants for the interactions between ortho CCH angle bends, between the CCX and the ortho CCH angle bends, between the CX stretch and the adjacent (ortho) CC stretches, and between the CC=O angle bend and the CCX angle bend were added to the zeroth approximation force field. The diagonal force constant for the CCX angle bend, the force constants for the interactions of this coordinate with the phenyl ring, and the force constants for the interactions

between the CX stretch and the phenyl ring were also defined independently of their phenyl counterparts in this force field. The initial values for these force constants were taken from analogous constants in benzene. This force field was refined using the Fletcher-Powell algorithm to minimize the difference between the observed and calculated frequencies. Again the two refinement strategies, a full field refinement and a substituent refinement followed by a phenyl refinement, were used.

TABLE XIII

IN-PLANE VALENCE FORCE CONSTANTS[a] FOR PHENOL

Mode	Type	Coordinate Involved	Initial Value	Individual Refinement	Joint Refinement
		Phenyl			
1	Stretch	C-C	6.433	6.427	6.392
2	Stretch	C-H	5.055	5.078	5.068
3	Bend	CCH	0.511	0.519	0.514
4	Bend	CCC	0.934	1.021	0.975
5	Stretch,stretch	o-CC,CC	0.750	0.694	0.739
6	Stretch,stretch	m-CC,CC	-0.316	-0.275	-0.319
7	Stretch,stretch	p-CC,CC	0.342	0.305	0.301
8	Stretch,bend	CC,CCC	0.164	0.272	0.260
9	Stretch,bend	CC,CCH	0.174	0.189	0.184
10	Bend,bend	o-CCC,CCC	-0.045	-0.010	-0.039
11	Stretch,stretch	o-CH,CH	0.017	0.058	0.059
12	Bend,bend	o-CCH,CCH	0.004	-0.016	0.006
		Hydroxyl			
13	Stretch	C-O	5.659	5.196	
14	Stretch	O-H	7.586	7.268	
15	Bend	COH	0.611	0.748	
16	Bend	CCO	1.300	0.983	
17	Stretch,stretch	CO,OH	0.005	0.003	
18	Stretch,bend	CO,COH	0.029	0.312	
19	Stretch,bend	OH,COH	0.000	0.035	
20	Stretch,bend	CC,CCO	0.174	0.248	
21	Stretch,stretch	CH,CO	0.017	-0.017	
22	Stretch,stretch	CO,CC	-0.115	0.984	
23	Bend,bend	COH,CCO	-0.005	-0.025	
24	Bend,bend	CCO,CCH	0.004	0.015	

[a]Units: stretch,stretch mdyne/Å; stretch,bend mdyne/rad; bend,bend mdyne Å/rad^2.

TABLE XIV

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE IN-PLANE VIBRATIONS OF PHENOL

Wavenumber, cm^{-1}		Error		Potential Energy Distribution		
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %		
3610	3609	1	0.02	OH(100)		
3086	3090	-4	-0.12	CH(97)		
3076	3075	1	0.03	CH(98)		
3061	3058	3	0.08	CH(99)		
3046	3041	5	0.17	CH(100)		
3022	3030	-8	-0.28	CH(101)		
1605	1605	0	0.03	CC(76)	CCH(19)	CCC(9)
1595	1594	1	0.06	CC(78)	CCH(24)	CCC(10)
1499	1498	1	0.09	CCH(65)	CC(33)	
1471	1475	-4	-0.28	CCH(61)	CC(31)	
1388	1378	10	0.76	CCH(65)	COH(17)	CC(14)
1345	1344	1	0.06	CC(112)	CCH(39)	
1251	1254	-3	-0.21	CO(48)	CCC(23)	CC(15)
1180	1186	-6	-0.54	COH(66)	CC(28)	CCH(10)
1168	1167	1	0.07	CCH(81)	CC(17)	
1152	1161	-9	-0.82	CCH(78)	CC(14)	
1071	1071	0	-0.01	CC(45)	CCH(36)	
1024	1019	5	0.51	CC(56)	CCH(26)	CCC(9)
1000	993	7	0.73	CC(58)	CCC(25)	
812	829	-17	-2.09	CCC(36)	CC(22)	CO(18)
618	619	-1	-0.13	CCC(67)	CCH(17)	CC(11)
530	506	24	4.58	CCC(49)	CO(22)	CCO(10)
416	416	0	0.07	CCO(82)		
Average Error		5	0.51			

[a]The internal coordinates are the phenyl CC stretches (CC), CH stretches (CH), CCH bends (CCH) and CCC bends (CCC), and the hydroxyl CO stretch (CO), OH stretch (OH), CCO bend (CCO) and the COH bend (COH).

The initial values of the force constants of the formyl group were taken both from an acetaldehyde force field developed by Cossee (67) and from a benzaldehyde force field constructed by Zwarich (37). Initial calculations using these force fields duplicated the observed frequencies adequately with reasonable potential energy distributions. Refinement of the force field using Zwarich's formyl force constants improved the fit between the observed and calculated frequencies, but caused an unacceptable shift in the potential energy distribution.

Refinement of the force field having initial formyl force constant values from Cossee's work resulted in both an improved frequency fit and an improved potential energy distribution.

The final benzaldehyde force field has twenty-seven force constants. Twelve of these force constants are associated with the phenyl coordinates and sixteen are associated with the formyl group and the interactions between the formyl and phenyl groups. Using this force field the twenty-five observed frequencies of benzaldehyde were calculated with an average error of 2.70 cm^{-1} or 0.227%. The force constants included in this field, along with their initial and final values are listed in Table XV. The observed and calculated frequencies of the normal modes and their potential energy distributions are presented in Table XVI.

Anisole. A thirty-two force constant modified valence force field for the in-plane modes of anisole was constructed using the same philosophy as that used to set up the in-plane phenol and benzaldehyde MVFF's. This force field comprised twelve phenyl force constants, sixteen force constants associated with the C-OCH_3 grouping and four force constants for the interactions between the two groups. The phenyl and phenyl-methoxyl interaction force constants were initially given values from the benzene force field. The initial values of the methoxyl force constants were from a force field for dimethyl ether developed by Snyder (68). The Fletcher-Powell minimization procedure was used to refine the initial field to minimize the difference between the observed and calculated frequencies. Both refinement strategies were used.

The best results were from the full field refinement. Using the final force field for the in-plane modes of anisole, the observed frequencies were

calculated with an average error of 2.56 cm^{-1} or 0.252%. The force constants included in this field and their initial and final values are listed in Table XVII. The observed and calculated frequencies and the potential energy distributions for these modes are given in Table XVIII.

TABLE XV

IN-PLANE VALENCE FORCE CONSTANTS[a] FOR BENZALDEHYDE

Mode	Type	Coordinate Involved	Initial Value	Individual Refinement	Joint Refinement
		Phenyl			
1	Stretch	C-C	6.433	6.372	6.392
2	Stretch	C-H	5.055	5.054	5.068
3	Bend	CCH	0.511	0.506	0.514
4	Bend	CCC	0.934	0.989	0.975
5	Stretch,stretch	o-CC,CC	0.750	0.802	0.739
6	Stretch,stretch	m-CC,CC	-0.316	-0.364	-0.319
7	Stretch,stretch	p-CC,CC	0.342	0.278	0.301
8	Stretch,bend	CC,CCC	0.164	0.256	0.260
9	Stretch,bend	CC,CCH	0.174	0.176	0.184
10	Bend,bend	o-CCC,CCC	-0.045	-0.046	-0.039
11	Stretch,stretch	o-CH,CH	0.017	0.058	0.059
12	Bend,bend	o-CCH,CCH	0.004	-0.004	0.006
		Formyl			
13	Stretch	C-C	4.500	4.572	
14	Stretch	C=O	10.772	10.574	
15	Stretch	C-H	4.243	4.038	
16	Bend	CCO	1.000	1.025	
17	Bend	CCH	0.811	0.209	
18	Bend	OCH	0.600	1.019	
19	Bend	CCC	0.934	1.154	
20	Stretch,stretch	CC,CO	0.750	0.959	
21	Stretch,stretch	CO,CH	0.000	-0.078	
22	Stretch,bend	CC,CCH	0.174	0.221	
23	Stretch,bend	CC,CCC	0.164	0.338	
24	Bend,bend	CCO,CCC	0.111	-0.135	
25	Stretch,stretch	CC,CC	0.700	0.494	
26	Bend,bend	o-CCC,CCH	0.004	-0.023	
27	Stretch,stretch	o-CC,CH	0.017	0.058	

[a]Units: stretch,stretch mdyne/Å; stretch,bend mdyne/rad; bend,bend mdyne Å/rad^2.

TABLE XVI

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE IN-PLANE VIBRATIONS OF BENZALDEHYDE

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
3088	3083	5	0.18	CH(97)
3065	3068	-3	-0.10	CH(98)
3045	3051	-6	-0.21	CH(99)
3035	3034	1	0.05	CH(100)
3026	3024	2	0.08	CH(101)
2737	2739	-2	-0.06	CH B(98)
1700	1698	2	0.10	CO(69) OCH(20)
1600	1605	-5	-0.33	CC(74) CCH(26) CCC(10)
1588	1584	4	0.23	CC(77) CCH(20)
1496	1487	9	0.63	CCH(58) CC(38)
1458	1457	1	0.06	CCH(48) CC(35)
1394	1393	1	0.06	OCH(48) CO(22) CCH(15)
1314	1319	-5	-0.42	CCH(89) CC(19)
1288	1286	2	0.17	CC(101) CCH(40)
1205	1206	-1	-0.08	CC B(37) CCH(23) CCC(21)
1168	1165	3	0.24	CC(54) CCH(52)
1162	1161	1	0.06	CCH(69) CC(19)
1072	1074	-2	-0.15	CCH(43) CC(41)
1023	1021	2	0.16	CC(33) CCH(29) CCC(28)
1002	1005	-3	-0.31	CC(61) CCC(13) CCH(9)
830	831	-1	-0.17	CC(29) CC B(19) CCC(18)
649	648	1	0.21	CCC(41) CCO(20) CC(9)
615	615	0	0.07	CCC(56) CC(14) CCH(14)
439	440	-1	-0.20	CCCB(27) CCC(20) CC B(20)
226	229	-3	-1.37	CCCB(52) CCO(40)
Average Error		3	0.23	

[a]The internal coordinates are the phenyl CC stretches (CC), CH stretches (CH), CCH bends (CCH) and CCC bends (CCC), and the formyl CC stretch (CCB), CH stretch (CHB), CO stretch (COB), CCC bend (CCCB), OCH bend (OCH) and CCO bend (CCO).

Out-of-plane Force Fields

Phenol. The modified valence force field used to calculate the fundamental out-of-plane frequencies of phenol consisted of seven phenyl force constants and two hydroxyl force constants. Also included were three force constants for interactions between the phenyl and hydroxyl groups: between the CX wag and the ortho CH wags, between the CX wag and the ortho CC torsions, and between the CX

torsion and the ortho CC torsions. Initial values of these force constants were taken from the benzene out-of-plane force field described in Chapter I and Zwarich's benzaldehyde calculations (37).

TABLE XVII

IN-PLANE VALENCE FORCE CONSTANTS[a] FOR ANISOLE

Mode	Type	Coordinate Involved	Initial Value	Individual Refinement	Joint Phenyl Refinement
		Phenyl			
1	Stretch	C-C	6.433	6.386	6.392
2	Stretch	C-H	5.055	5.074	5.068
3	Bend	CCH	0.511	0.515	0.514
4	Bend	CCC	0.934	0.971	0.975
5	Stretch,stretch	o-CC,CC	0.750	0.748	0.739
6	Stretch,stretch	m-CC,CC	-0.316	-0.323	-0.319
7	Stretch,stretch	p-CC,CC	0.342	0.269	0.301
8	Stretch,bend	CC,CCC	0.164	0.250	0.260
9	Stretch,bend	CC,CCH	0.174	0.183	0.184
10	Bend,bend	o-CCC,CCC	-0.045	-0.010	-0.039
11	Stretch,stretch	o-CH,CH	0.017	0.057	0.059
12	Bend,bend	o-CCH,CCH	0.004	-0.002	0.006
		Methoxyl			Joint IP/OOP
13	Stretch	C-O	5.152	5.169	5.172
14	Stretch	O-C	4.992	4.974	4.972
15	Stretch	C-H	4.689	4.602	4.623
16	Bend	COC	1.425	1.450	1.453
17	Bend	OCH	0.880	0.872	0.867
18	Bend	HCH	0.508	0.518	0.520
19	Bend	CCO	1.148	1.159	1.160
20	Stretch,stretch	CH,CH	-0.057	0.006	-0.001
21	Stretch,stretch	CO,OC	0.319	0.305	0.303
22	Stretch,bend	CO,COC	0.318	0.317	0.316
23	Bend,bend	OCH,OCH	-0.023	-0.030	-0.029
24	Bend,bend	COC,OCH	-0.262	-0.264	-0.262
25	Bend,bend	COC,OCH	0.078	0.080	0.079
26	Stretch,stretch	CC,CO	0.439	0.428	0.426
27	Stretch,bend	CC,CCO	0.297	0.300	0.299
28	Stretch,stretch	o-CH,CO	0.022	0.021	0.021
29	Bend,bend	o-CCH,CCO	-0.016	-0.018	-0.018
30	Stretch,bend	CO,CCO	0.611	0.597	0.594
31	Bend,bend	COC,CCO	0.497	0.475	0.474
32	Stretch,bend	OC,OCH	0.272	0.271	0.271

[a]Units: stretch,stretch mdyne/Å; stretch,bend mdyne/rad; bend,bend mdyne Å/rad^2.

TABLE XVIII

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE IN-PLANE MODES OF ANISOLE

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
3093	3088	5	0.16	CH(97)
3069	3074	-5	-0.15	CH(98)
3055	3057	-2	-0.07	CH(99)
3037	3040	-3	-0.09	CH(100)
3033	3029	4	0.12	CH(101)
2945	2942	3	0.09	CHM(100)
2833	2833	0	0.02	CHM(99)
1600	1602	-2	-0.15	CC(75) CCH(27) CCC(10)
1587	1584	3	0.19	CC(79) CCH(22)
1497	1493	4	0.25	CCH(60) CC(37)
1468	1468	0	0.03	OCH(57) HCH(35)
1455	1457	-2	-0.12	CCH(41) CC(26) HCH(17) OCH(12)
1441	1439	2	0.13	HCH(66) OCH(15) CCH(12)
1336	1336	0	-0.04	CCH(87) CC(28)
1304	1304	0	-0.03	CC(104) CCH(36)
1248	1243	5	0.37	CO(51) CCH(15) CC(12) CCC(11)
1181	1180	1	0.07	CCH(60) CC(40)
1172	1171	1	0.12	CCH(73) CC(16)
1112	1112	0	-0.02	OCH(69) HCH(14)
1078	1084	-6	-0.54	CCH(36) CC(33) OC(12)
1040	1043	-3	-0.28	OC(59) CC(14) CCH(11)
1021	1016	5	0.47	CC(42) CCH(28) CCC(20)
995	996	-1	-0.06	CC(52) CCC(24)
784	782	2	0.21	CCC(28) CO(24) CC(22)
615	618	-3	-0.43	CCC(65) CCH(17)
553	549	4	0.76	COC(43) CCC(34) CCO(22) CC(10)
443	445	-2	-0.56	CCO(31) COC(20) CCC(14) CC(11) CO(10)
266	262	4	1.52	CCO(41) COC(30)
Average Error		3	0.25	

[a]The internal coordinates are the phenyl CC stretches (CC), CH stretches (CH), CCH bends (CCH) and CCC bends (CCC), and the methoxyl CO stretch (CO), OC stretch (OC), CH stretches (CHM), CCO bends (CCO), COC bend (COC), OCH bends (OCH) and HCH bends (HCH).

The initial force field was refined in the usual two ways: one, refining the substituent and phenyl portions of the force field separately and two,

refining the entire force field simultaneously. The frequency of vibration 10a, being unknown, was at first omitted from these refinements. The purpose of the initial calculations was to observe the behavior of the frequency assigned to vibration 10a on refinement. The information gained from these calculations was to be used in the assignment of this band. Based on these calculations and the depolarization ratios of the Raman bands, vibration 10a was assigned at a frequency of 818 cm^{-1}. The specifics of this assignment are discussed in the section on spectral assignments.

The initial force field for phenol was refined using a complete set of observed out-of-plane frequencies. The results of the refinements were not satisfactory. Though the calculated frequencies closely approximated the experimental frequencies, the potential energy distributions calculated using the refined fields were not acceptable. Various additional force constants were evaluated (20,73). Defining two different diagonal force constants for the CC torsions, one for the torsions adjacent to the substituent carbon, and one for the remaining torsions, gave the desired results. The observed frequencies were calculated with an average error of 1.89 cm^{-1} or 0.300%. The calculated potential energy distribution was found to be reasonable. The force constants included in this field and their initial and final values are listed in Table XIX. The observed and calculated frequencies and their potential energy distributions are given in Table XX.

Benzaldehyde. A fourteen parameter modified valence force field was initially used to calculate the fundamental frequencies of the out-of-plane modes of benzaldehyde. This force field comprised the seven phenyl force constants from the benzene field described in Chapter I, four diagonal force constants for the C-CHO grouping, and three force constants for interactions between the two

groups. This last set included constants for the interaction between the CX out-of-plane wag and the adjacent CC torsions, between the CX torsion and the adjacent CC torsions, and between the CX wag and the adjacent (ortho) CH wags. Initial values of the force constants for the phenyl group and for the interaction constants between the phenyl and formyl groups were taken from the benzene out-of-plane force field. Two different sets of initial force constants were used for the formyl force constants: those used by Zwarich (37) in his calculations, and a set derived from analogous benzene force constants. Combinations of these two sets of substituent force constant values were also evaluated.

TABLE XIX

OUT-OF-PLANE VALENCE FORCE CONSTANTS[a] FOR PHENOL

Mode	Type	Coordinate Involved	Initial Value	Individual Refinement	Joint Refinement
		Phenyl			
1	Wag	H-CCC	0.3228	0.3336	0.3295
2	Torsion	CCCH/CCCX	0.2375	0.2522	0.2372
3	Torsion	CCCH/CCCH	0.2375	0.2244	0.2371
4	Wag,wag	o-H-CCC,H-CCC	0.0183	0.0149	0.0197
5	Wag,wag	m-H-CCC,H-CCC	-0.0235	-0.0077	-0.0110
6	Wag,wag	p-H-CCC,H-CCC	-0.0233	-0.0065	-0.0109
7	Wag,torsion	H-CCC,CCCC	0.0378	0.0451	0.0407
8	Torsion,torsion	o-CCCC,CCCC	-0.0770	-0.0771	-0.0712
		Hydroxyl			
9	Wag	O-CCC	0.3228	0.4164	
10	Torsion	CC-OH	0.0360	0.0424	
11	Wag,wag	o-O-CCC,H-CCC	0.0183	0.0619	
12	Wag,torsion	O-CCC,CCCC	0.0378	-0.0447	
13	Torsion,torsion	o-CCOH,CCCC	-0.0100	0.0278	

[a]Units: mdyne Å/rad^2.

As it was unknown, the frequency of the out-of-plane wag of the aldehyde hydrogen was excluded from the initial refinement of the benzaldehyde out-of-plane

force field. As in the phenol calculations, these initial refinements were performed to observe the behavior of the frequency calculated for this mode on refinement to aid in the assignment of this band. Based on these calculations, and on other data discussed in the section on spectral assignments, the out-of-plane formyl hydrogen wag was assigned to a weak band at 1008 cm^{-1} in the IR spectrum.

TABLE XX

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE OUT-OF-PLANE VIBRATIONS OF PHENOL

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
986	986	0	0.05	WAG(106) TOR(23)
958	956	2	0.21	WAG(99) TOR(26)
890	896	-6	-0.67	WAG(95) TOR(21)
818	814	4	0.46	WAG(91) TOR(22)
756	757	-1	-0.11	WAG(94)
690	689	1	0.09	TOR(38) WAGO(25) WAG(12)
509	513	-4	-0.70	WAGO(63) TOR(18)
416	416	0	-0.10	TOR(46) WAG(13)
309	309	0	0.05	TORO(80) TOR(20)
242	243	-1	-0.60	TOR(48) TORO(14) WAG(11)
Average Error		2	0.30	

[a]The internal coordinates are the phenyl wags (WAG) and torsions (TOR), and the hydroxyl wag (WAGO) and torsion (TORO).

Prior to refining the initial force field to the full set of observed frequencies, the force field was adjusted to include two different diagonal force constants for the CC torsions. As in phenol, one of these force constants accounted for the torsions of the CC bonds adjacent to the substituted carbon, and the other was for the remaining ring torsions. This force field was then refined to the observed frequencies. The best fit and potential energy distribution resulted from a substituent refinement followed by a phenyl refinement.

The average error between the observed frequencies and those calculated using this field is 1.3 cm^{-1} or 0.34%. Definitions of the force constants used in this field together with their initial and final values are presented in Table XXI. The frequencies and potential energy distribution calculated by the final force field are listed in Table XXII.

TABLE XXI

OUT-OF-PLANE VALENCE FORCE CONSTANTS[a] FOR BENZALDEHYDE

Mode	Type	Coordinate Involved	Initial Value	Individual Refinement	Joint Refinement
		Phenyl			
1	Wag	H-CCC	0.3336	0.3360	0.3295
2	Torsion	CCCH/CCCX	0.2522	0.2505	0.2372
3	Torsion	CCCH/CCCH	0.2244	0.2380	0.2371
4	Wag,wag	o-H-CCC,H-CCC	0.0149	0.0179	0.0197
5	Wag,wag	m-H-CCC,H-CCC	-0.0077	-0.0164	-0.0110
6	Wag,wag	p-H-CCC,H-CCC	-0.0065	-0.0202	-0.0109
7	Wag,torsion	H-CCC,CCCC	0.0451	0.0404	0.0407
8	Torsion,torsion	o-CCCC,CCCC	-0.0650	-0.0666	-0.0712
		Formyl			
9	Wag	C-CCC	0.3228	0.3217	
10	Wag	O=CCH	0.0650	0.0622	
11	Wag	H-CCO	0.3228	0.3193	
12	Torsion	CCCO/CCCH	0.0000	0.1081	
13	Wag,wag	H-CCC,C-CCC	0.0378	0.0142	
14	Wag,torsion	C-CCC,CCCC	0.0378	-0.0009	
15	Torsion,torsion	CCCO,CCCC	0.0000	0.0135	

[a]Units: mdyne Å/rad^2.

Anisole. The modified valence force field for the A" modes of anisole contains twenty force constants. Eight of these are phenyl force constants, three are interaction constants between the phenyl and methoxyl groups and nine are associated with the C-OCH_3 group. Of the nine force constants for the methoxyl group, four are for the CX out-of-plane wag and the two torsions, and five are due to the CH stretches, HCH bends and OCH bends. These last five

force constants are also present in the force field for the A' vibrations of the methoxyl group. Initial values for these force constants were taken to be those of analogous constants in benzene, methanol, and dimethyl ether force fields.

TABLE XXII

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE OUT-OF-PLANE VIBRATIONS OF BENZALDEHYDE

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
1008	1013	-5	-0.48	WAG(50) WAGH(40) TOR(9)
989	989	0	0.01	WAG(67) WAGH(27) TOR(18)
962	967	-5	-0.50	WAG(97) TOR(27)
924	919	5	0.56	WAG(76) TOR(18) WAGH(13)
851	854	-3	-0.39	WAG(83) TOR(20)
746	746	0	-0.02	WAG(97)
689	690	-1	-0.13	TOR(42) WAG(13) WAGC(12)
451	449	2	0.45	WAGC(54) TOR(26)
410	407	3	0.67	TOR(54) WAG(15)
237	240	-3	-1.20	TOR(39) TORC(24) WAG(10) WAGC(10)
128	126	2	1.72	TORC(70) TOR(11)
Average Error		3	0.56	

[a]The internal coordinates are the phenyl wags (WAG) and torsions (TOR), and the formyl wag (WAGC), CH wag (WAGH) and torsion (TORC).

Although the CH stretching modes and the HCH and OCH bending modes of the methoxyl group have been identifed, their division into A' and A" modes varies. To aid in the assignment of these methoxyl modes, normal coordinate calculations were performed for methanol and for a methanol-like molecule with a point mass of 77 replacing the hydroxyl hydrogen. In these calculations the frequencies of the A" modes of the CH stretching and OCH and HCH bending deformations did not shift. The A" modes were assigned using this observation, the positions of these bands in CH_3OH, initial anisole calculations and Raman depolarization ratios. The CH stretch was assigned to a band at 2957 cm^{-1}, the HCH bend at 1456 cm^{-1} and the OCH bend at 1154 cm^{-1}.

The anisole out-of-plane force field was refined to the observed frequencies. Using the final set of force constants, the observed frequencies were calculated with an average error of 2.04 cm-1 or 0.671% and a reasonable potential energy distribution (Table XXIII). Force constant definitions and their initial and final values are given in Table XXIV.

TABLE XXIII

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE OUT-OF-PLANE MODES OF ANISOLE

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
2957	2951	6	0.21	CH(99)
1441	1441	0	-0.01	HCH(78) OCH(22)
1153	1155	-2	-0.17	OCH(77) HCH(21)
978	976	2	0.19	WAG(108) TOR(25)
960	960	0	0.01	WAG(99) TOR(26)
885	885	0	-0.01	WAG(98) TOR(24)
820	822	-2	-0.21	WAG(90) TOR(21)
757	757	0	0.02	WAG(95)
692	694	-2	-0.25	TOR(33) WAGC(28) WAG(18)
513	515	-2	-0.40	WAGC(62) TOR(18)
415	414	1	0.32	TOR(53) WAG(12)
285	290	-5	-1.71	TORO(56) TOR(31)
214	223	-9	-4.27	TORO(39) TOR(22)
108	110	-2	-1.76	TORC(105) TORO(13) TOR(9)
Average Error		2	0.68	

[a]The internal coordinates are the phenyl wags (WAG) and torsions (TOR), and the methoxyl wag (WAGO), CH stretch (CH), OCH bend (OCH), HCH bend (HCH), C-OCH_3 torsion (TORO) and CO-CH_3 torsion (TORC).

The in-plane and out-of-plane force fields of anisole were initially refined separately. However, they are not independent; they share five force constants. Therefore, they were refined together. Refinements were carried out over the full fields, over just the five force constants in question and over the substituent force fields. The substituent refinement gave the best results. The average error for the in-plane calculations was 2.72 cm-1 or 0.256%, and for

the out-of-plane calculations 1.11 cm^{-1} or 0.137% (Tables XVII, XXIV, XXV and XXVI).

TABLE XXIV

OUT-OF-PLANE VALENCE FORCE CONSTANTS[a] FOR ANISOLE

Mode	Type	Coordinate Involved	Initial Value	Individual Refinement	Joint Phenyl Refinement
		Phenyl			
1	Wag	H-CCC	0.3228	0.3372	0.3295
2	Torsion	CCCH/CCCX	0.2375	0.2503	0.2372
3	Torsion	CCCH/CCCH	0.2375	0.2265	0.2371
4	Wag,wag	o-H-CCC,H-CCC	0.0183	0.0178	0.0197
5	Wag,wag	m-H-CCC,H-CCC	-0.0235	-0.0105	-0.0110
6	Wag,wag	p-H-CCC,H-CCC	-0.0233	-0.0062	-0.0109
7	Torsion,torsion	o-CCCC,CCCC	-0.0770	-0.0718	-0.0712
8	Torsion,wag	CCCC,H-CCC	0.0378	0.0457	0.0407
		Methoxyl			Joint IP/OOP
9	Wag	CCC-OCH	0.4012	0.3899	0.3870
10	Torsion	CC-OCH	0.0418	0.1138	0.1074
11	Torsion	CO-CH	0.0800	0.1225	0.1081
12	Torsion,wag	CCCC,O-CCC	0.0619	0.0175	0.0181
13	Torsion,torsion	CCCC,CC-OC	0.0278	0.0433	0.0472
14	Wag,wag	o-H-CCC,O-CCC	-0.0447	-0.0760	-0.0768
15	Torsion,torson	CCOC,COCH	0.0278	0.0433	0.0472

[a]Units: mdyne Å/rad^2.

Joint Refinements

The force fields for the monosubstituted benzene derivatives were developed to be transferred to the force fields for the disubstituted benzene derivatives. Both the in-plane and out-of-plane force fields for the monosubstituted compounds comprise a phenyl and substituent component. The form of the phenyl components, i.e., the internal coordinate and force constant definitions, are the same for each of these compounds. To generalize these phenyl force fields, the phenyl portions of the force fields for phenol, benzaldehyde, and anisole were refined simultaneously.

TABLE XXV

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE IN-PLANE MODES OF ANISOLE, A' AND A" REFINEMENT

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
3093	3088	5	0.16	CH(97)
3069	3074	-5	-0.15	CH(98)
3055	3057	-2	-0.07	CH(99)
3037	3040	-3	-0.09	CH(100)
3033	3029	4	0.12	CH(101)
2945	2951	-6	-0.21	CHM(99)
2833	2835	-2	-0.06	CHM(100)
1600	1603	-3	-0.17	CC(75) CCH(27) CCC(10)
1587	1584	3	0.18	CC(79) CCH(22)
1497	1493	4	0.24	CCH(60) CC(37)
1468	1467	1	0.06	OCH(55) HCH(35)
1455	1457	-2	-0.13	CCH(40) CC(25) HCH(19) OCH(13)
1441	1440	1	0.05	HCH(65) OCH(14) CCH(13)
1336	1336	0	-0.04	CCH(87) CC(28)
1304	1305	-1	-0.05	CC(104) CCH(36)
1248	1244	4	0.34	CO(51) CCH(15) CC(12) CCC(11)
1181	1180	1	0.07	CCH(60) CC(40)
1172	1171	1	0.12	CCH(73) CC(16)
1112	1110	2	0.15	OCH(69) HCH(14)
1078	1084	-6	-0.54	CCH(36) CC(33) OC(12)
1040	1043	-3	-0.28	OC(59) CC(14) CCH(11)
1021	1016	5	0.47	CC(42) CCH(28) CCC(20)
995	996	-1	-0.06	CC(52) CCC(24)
784	782	2	0.20	CCC(28) CO(24) CC(22)
615	618	-3	-0.44	CCC(65) CCH(17)
553	549	4	0.69	COC(43) CCC(34) CCO(22) CC(10)
443	446	-3	-0.58	CCO(31) COC(19) CCC(14) CC(11) CO(10)
266	262	4	1.48	CCO(41) COC(30)
Average Error		3	0.26	

[a]The internal coordinates are the phenyl CC stretches (CC), CH stretches (CH), CCH bends (CCH) and CCC bends (CCC), and the methoxyl CO stretch (CO), OC stretch (OC), CH stretches (CHM), CCO bends (CCO), COC bend (COC), OCH bends (OCH) and HCH bends (HCH).

The in-plane problem for all three compounds was set up using the same twelve phenyl force constants. The values of this initial set of phenyl force constants were taken from the benzene force field. The substituent force

constants were set at the final values attained in the individual refinements. The out-of-plane problem was handled analogously.

TABLE XXVI

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE OUT-OF-PLANE MODES OF ANISOLE, A' AND A" REFINEMENT

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
2957	2951	6	0.21	CH(99)
1441	1441	0	-0.01	HCH(78) OCH(22)
1153	1155	-2	-0.17	OCH(77) HCH(21)
978	976	2	0.20	WAG(108) TOR(25)
960	960	0	0.04	WAG(99) TOR(26)
885	885	0	0.03	WAG(98) TOR(24)
820	821	-1	-0.18	WAG(90) TOR(21)
757	757	0	0.03	WAG(95)
692	692	0	-0.03	TOR(33) WAGC(27) WAG(19)
513	513	0	0.04	WAGC(63) TOR(18)
415	414	1	0.26	TOR(53) WAG(12)
285	284	1	0.21	TORO(45) TOR(36)
214	214	0	-0.10	TORO(51) TOR(18)
108	108	0	-0.38	TORC(103) TOR(9)
Average Error		1	0.14	

[a]The internal coordinates are the phenyl wags (WAG) and torsions (TOR), and the methoxyl wag (WAGO), CH stretch (CH), OCH bend (OCH), HCH bend (HCH), C-OCH_3 torsion (TORO) and CO-CH_3 torsion (TORC).

The phenyl force constants were refined to minimize the differences between the observed and calculated frequencies for all three monosubstituted benzene derivatives. Using the refined force field for both the in-plane and out-of-plane problems, the observed frequencies of the three compounds were adequately calculated, though not as accurately as in the individual refinements. Subsequent refinement of the substituent force constants does not significantly improve the fit of the calculated to observed frequencies. The average errors of the calculated in-plane frequencies of phenol, benzaldehyde and anisole are 6.66 cm^{-1} or 0.664%, 4.83 cm^{-1} or 0.423%, and 4.00 cm^{-1} or 0.381%. The average errors of the

out-of-plane frequencies of these compounds are 4.40 cm^{-1} or 0.706%, 5.54 cm^{-1} or 0.837% and 4.87 cm^{-1} or 0.764%, respectively. Comparison of the line representations of the observed and calculated spectra shows the accuracy of fit (Fig. 8-10).

The force constants for the in-plane and out-of-plane vibrations of the phenyl ring, developed in the joint refinement, are used in the normal coordinate calculations for the di- and trisubstituted benzenes.

EVALUATION OF SOLUTION

A force field was accepted in this investigation if it contained reasonably valued force constants, and if its use resulted in accurate calculation of the observed frequencies (i.e., a low average error) and the calculation of a reasonable potential energy distribution.

Average errors of 5-15 cm^{-1} between the observed and calculated frequencies are common and accepted in the literature. The average errors of the calculated frequencies for the final force fields, as cited in the previous section, are all less than 7 cm^{-1}. Comparison of the differences between the calculated and observed frequencies show the errors to be random, that is, no one frequency is consistently too high or too low.

A potential energy distribution was considered to be reasonable if it agreed with assignments made on the basis of group frequency data, deuteration studies and information gleaned from the vibrational spectra of the compound. The potential energy distributions calculated using the final force fields correctly assign those bands that have accepted assignments.

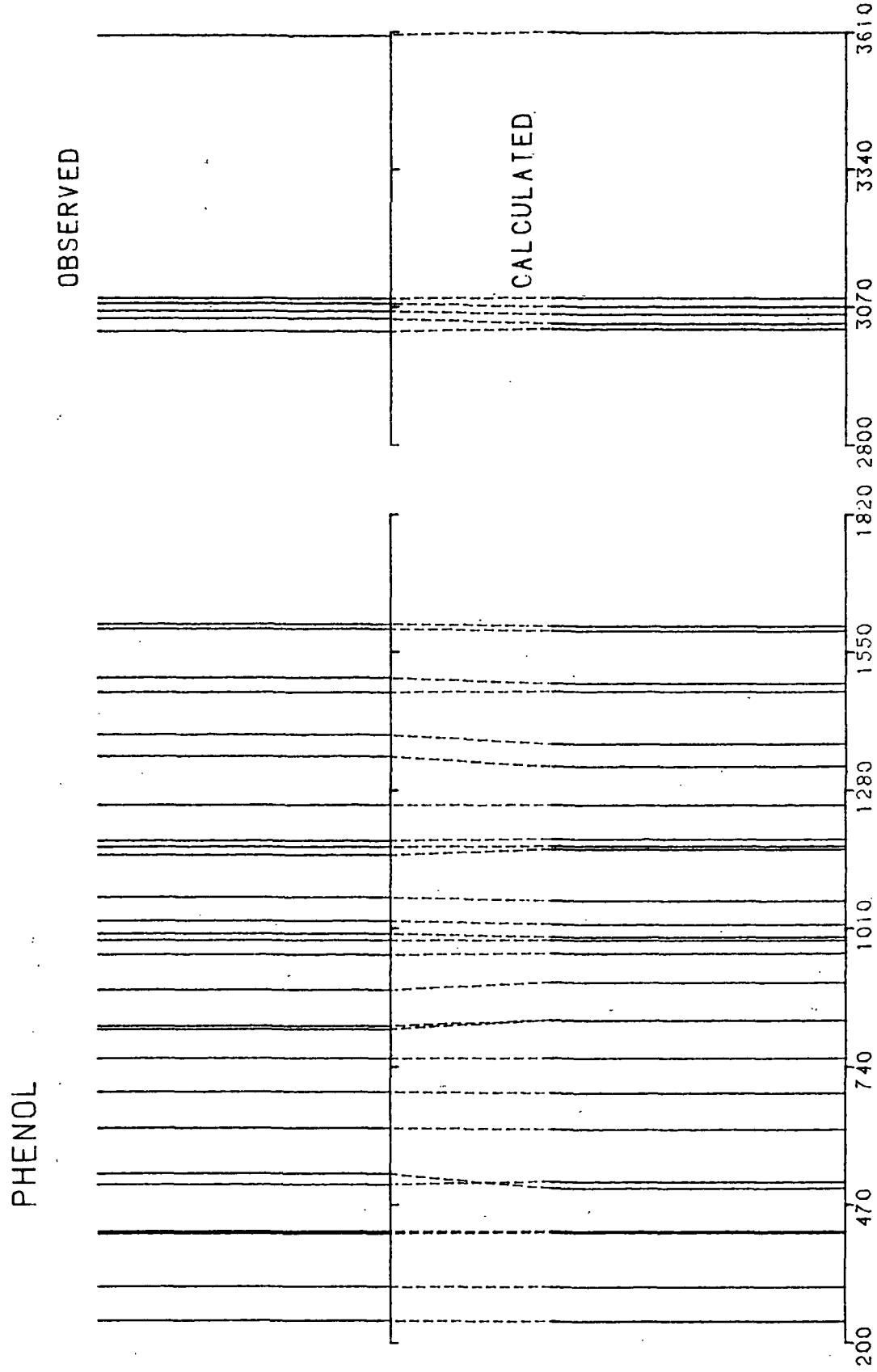


Figure 8. Comparison of the observed to the calculated spectra of phenol.

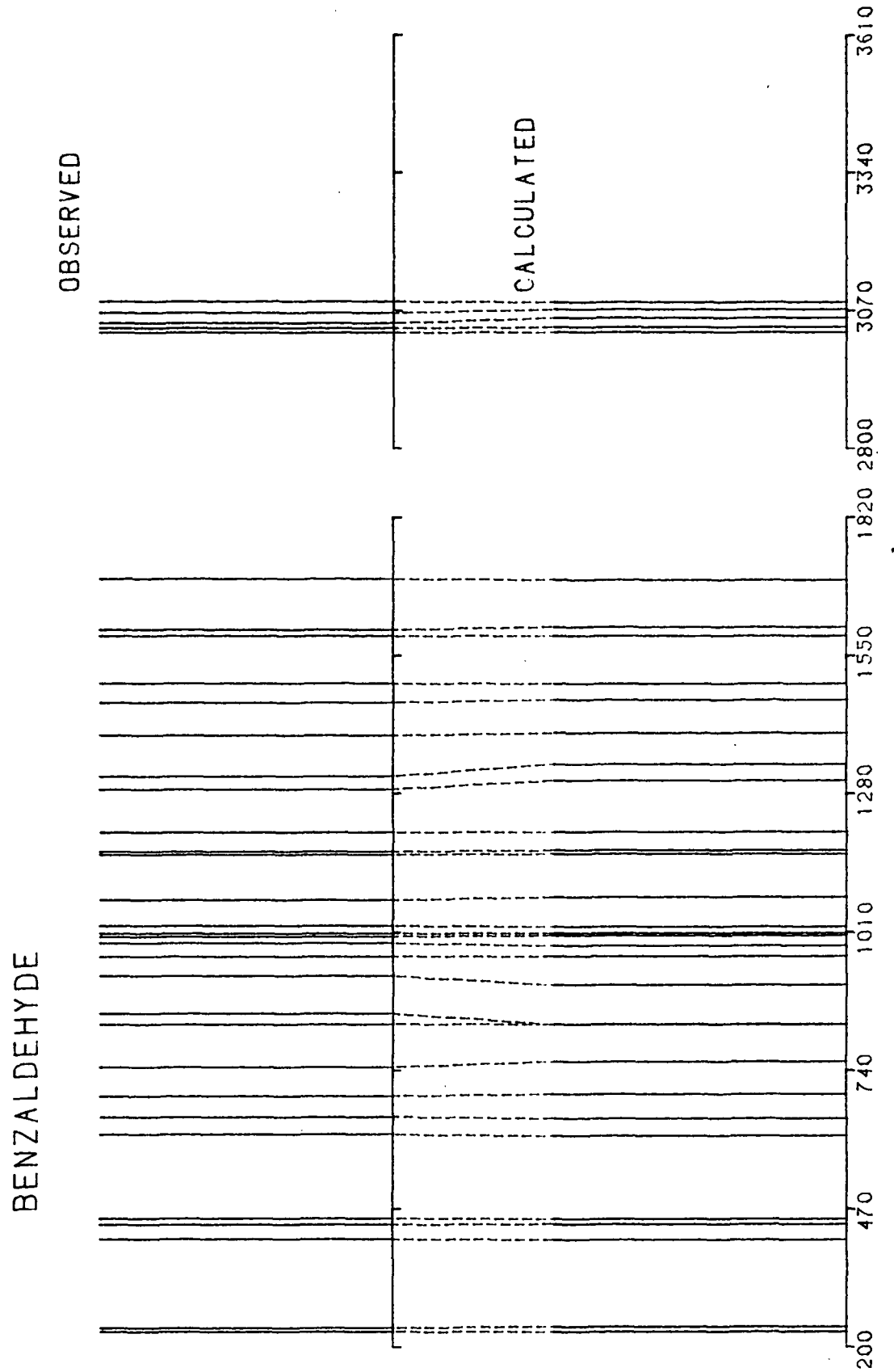


Figure 9. Comparison of the observed to the calculated wavenumbers of benzaldehyde.

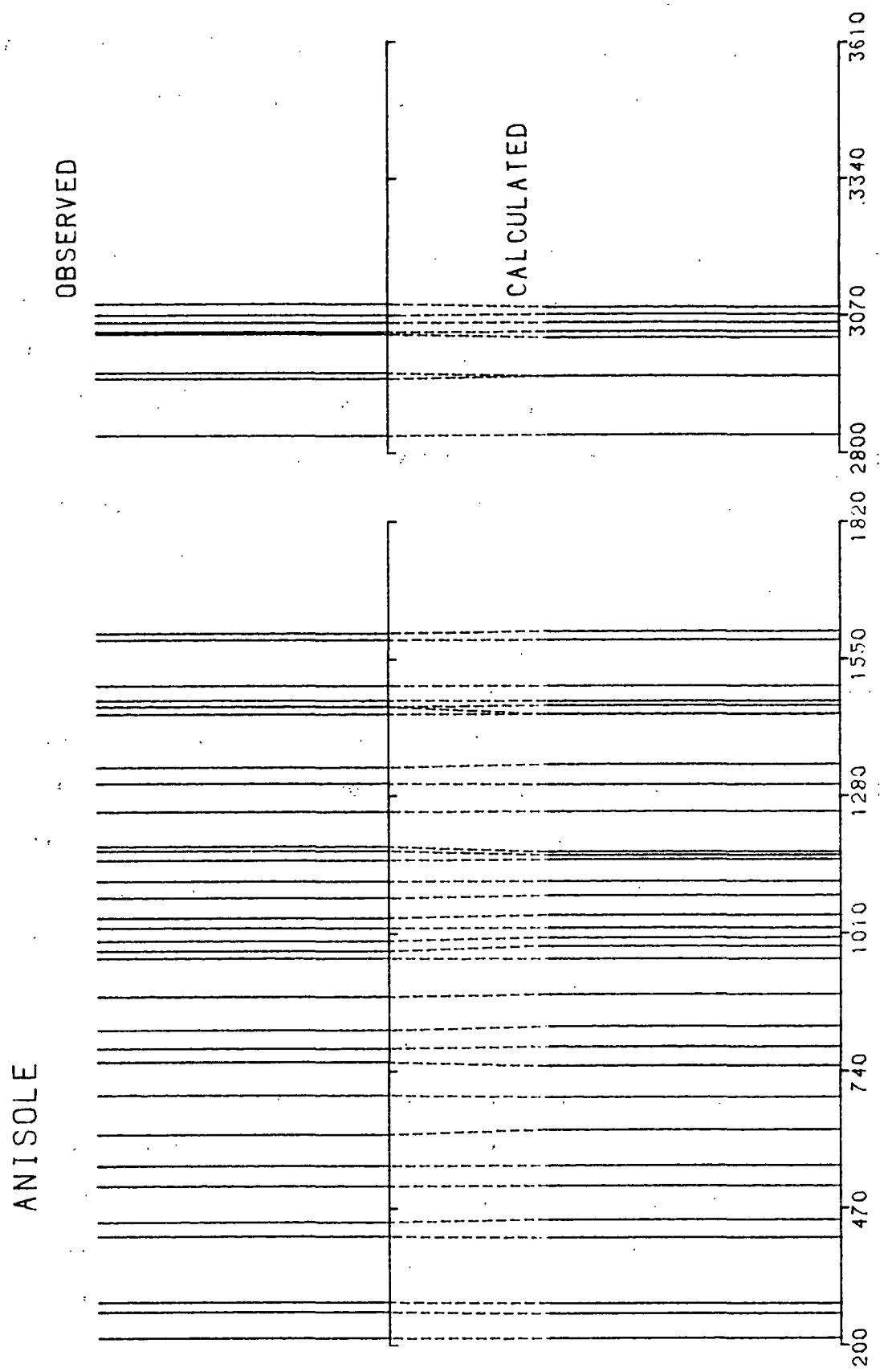


Figure 10. Comparison of the calculated to the observed spectra of anisole.

In addition to accurately determining the observed frequencies and a reasonable potential energy distribution, the refined force field should include reasonable force constant values. 'Reasonable' values for the force constants were earlier defined to be force constant values that are similar to those found for that particular interaction in a force field for a similar molecule or grouping. Small changes are to be expected due to differing internal coordinate definitions. Owing to the use of force constants from appropriate substituent force fields as initial values, only small changes in these substituent force constants would be expected. As they were either set to zero or only approximated by seemingly appropriate benzene force constants, larger changes in the interaction force constants between the substituent and phenyl groups are anticipated. Most of the force constants that did change significantly fall in this latter category.

All of the in-plane interaction constants between the hydroxyl and phenyl groups of the phenol force field changed to some degree (Table XIII). The largest change was observed in force constant 22, the interaction constant between the ortho CO and CC stretches. The initial value, -0.115 mdyne/Å, was the value of an analogous o-CC,CH stretching interaction constant. Due to the size and nature of the oxygen atom (22) a more appropriate initial value would be that of the interaction between o-CC,CC bond stretches (0.75 mdyne/Å). Refinements using this initial value result in a value of 0.8-0.9 mdyne/Å for this force constant, which is similar to the 0.984 mdyne/Å value found in the original refinement. The other major change was in the CO,COH interaction force constant (No. 18, Table XIII). This force constant refined to a final value of 0.312 mdyne/rad from an initial value of 0.029 mdyne/rad. The initial value of this force field was from Gebhardt's methanol force field (66). Comparison to other values for this force constant (74,75,76,77) show that with approximately

the same values for the other hydroxyl force constants, the values for this force constant range from 0.029 to 0.42 mdyne/rad. The final value of this force constant, 0.312 mdyne/rad, falls in this range.

The initial values of the hydroxyl force constants and of the hydroxyl-phenyl interaction force constants in the out-of-plane force field for phenol were all approximated. The former were from Zwarich's benzaldehyde force field (37), and the latter from the phenyl force field. Changes in the force constant values were therefore expected. The final values of these force constants are consistent with those found by Bist (33) in his out-of-plane force field for phenol. The changes observed in the phenyl force constants can be explained by the changes in the definitions of the internal coordinates.

Comparison of the initial and final force constants for the in-plane vibrations of benzaldehyde show significant changes in two of the diagonal formyl force constants and in most of the phenyl-formyl interaction force constants. The diagonal force constants for the CCH and OCH angle bends had initial values of 0.811 and 0.600 mdyne Å/rad^2 and final refined values of 0.209 and 1.019 mdyne Å/rad^2. The initial values of these force constants were from Zwarich's benzaldehyde force field (37). Zwarich used Cossee's acetaldehyde force constants with a few "rather arbitrary alterations in bond stretching and angle bending force constants in order to compensate for force constant variations with geometry" (37). Cossee's original values for these force constants were 0.435 and 0.827 mdyne Å/rad^2, respectively, which are more in line with the final values of this refinement. Since the initial values of the phenyl-formyl interaction constants were approximate, changes in these values were expected on refinement of the field.

The initial values of the diagonal formyl force constants and the formyl-phenyl interaction constants in the out-of-plane force field of benzaldehyde were set to zero or approximated by appropriate phenyl force constants. The final values of these force constants were consistent with the values used by Zwarich (37) in his benzaldehyde out-of-plane force field.

The initial values of the A' methoxyl force constants in the anisole force field were from a dimethyl ether force field developed by Snyder (68). The values for the A' methoxyl-phenyl force constants were taken from analogous phenyl force constants. Only one of these force constants changed substantially on refinement. The value of the CH,CH interaction constant (No. 20, Table XVII) changed from -0.057 to -0.001 mdyne/Å. Values for this force constant in methoxyl force fields range from 0.102 to -0.057 mdyne/Å (66,68,74,76,77). The final value of force constant 20 falls in this range.

The A" methoxyl force constants and the methoxyl-phenyl interaction constants were given initial values of appropriate force constants from the phenol force field or a methanol force field. The final values, though slightly different than the initial, are consistent with the results for the other monosubstituted compounds.

INTERPRETATION OF SPECTRA

The potential energy distributions calculated using the final force fields aid in the assignment of those bands that have several different literature assignments. Once assigned, the frequencies and intensities of the phenyl modes are analyzed to ascertain the effect of monosubstitution on the fundamental modes of benzene. The results of this analysis and the spectral assignments are discussed in this section.

Spectral Assignments

Assignment of the infrared and Raman spectra of the monosubstituted benzene derivatives in this study is based on the assignments of the spectra reported in the literature, on the depolarization ratios of the Raman bands and on the normal coordinate calculations. The bands that have been inconsistently assigned in the literature and the assignment of these bands in this investigation are discussed in this section.

Phenol

The assignments of the fundamental modes of phenol are listed in Table XXVII. The phenol modes corresponding to benzene in-plane modes 3 and 14, the COH in-plane deformation and out-of-plane benzene vibration 10a have each been assigned to a variety of frequencies. In this investigation, these three in-plane modes of phenol have been assigned based on the potential energy distributions. The out-of-plane mode has been assigned using the depolarization ratios and the normal coordinate calculations. Reversal of the assignments of the in-phase and out-of-phase breathing modes (vibrations 1 and 12) is also proposed.

The ring stretching mode derived from benzene mode 14 is considered to be coupled with the OH bending mode. Evans (26) assigned mode 14 to a band at 1344 cm^{-1} in Fermi resonance with the combination 814 + 530 = 1344 cm^{-1}. Green (27) ascribed the doublet at 1332-1344 cm^{-1} to fundamental mode 14 (assigned at 1333 cm^{-1}) in Fermi resonance with the combination 502 + 825 = 1327 cm^{-1}. Green also attributed some OH bending character to the band assigned as mode 14 (28). Pinchas (29) asserted that these interpretations of this doublet were incorrect based on the vibrational spectra of ^{18}O-phenol. The frequency of this doublet is virtually unchanged in ^{18}O-phenol, but the frequencies of the combination

TABLE XXVII

ASSIGNMENT OF THE NORMAL MODES OF PHENOL

Infrared, cm^{-1}	Raman, cm^{-1}	Assignment
	242 m[a]	16b A" ring deformation
	309 w	A" COH torsion
	416 w	16a A" ring deformation
		9b A' CX bend
511 m	509 w	10b A" CX bend
533 m	531 m	6a A' ring deformation
618 w	618 m	6b A' ring deformation
691 vs	690 vw	4 A" ring deformation
753 vs	756 w	11 A" wag
810 s	812 s	1 A' ring deformation
	818 m	10a A" wag
887 m	890 vw	17b A" wag
959 vw	958 vw	17a A" wag
978 vw	986 m	5 A" wag
1000 vw	1001 vs	12 A' ring deformation
1024 m	1026 s	18a A' CH bend
1071 m	1073 w	18b A' CH bend
1153 m	1154 m	15 A' CH bend
1169 s	1170 m	9a A' CH bend
1180 sh	1192 w	A' COH bend
	1252 m	13 A' CX stretch
1345 m		14 A' CC stretch
1389 sh	1380 w	3 A' CH bend
1473 vs	1470 w	19b A' CC stretch
1499 vs	1500 w	19a A' CC stretch
1596 vs	1594 m	8a A' CC stretch
1604 sh	1606 m	8b A' CC stretch
3024 m	3022 vw	7a A' CH stretch
3046 m		20b A' CH stretch
	3061 w	20a A' CH stretch
3076 m		7b A' CH stretch
3093 m	3086 vw	2 A' CH stretch
3348 s		A' OH stretch, polymer
	3602 w	A' OH stretch, monomer

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

bands are substantially shifted. Green's combination shifts to 506 + 841 cm^{-1}, and Evan's shifts to 530 + 802 cm^{-1}. Pinchas proposed that this band belongs to the 1000 + 320 cm^{-1} combination. Wilson (30), studying the spectra of phenol vapor, assigned a band of medium intensity at 1388 cm^{-1} in the Raman spectrum to this ring stretching mode. Wilson argued that both this band and the band at

1343 cm^{-1} in the IR spectrum could be accounted for by an appropriate choice of combination or overtone bands. Since overtone and combination bands are generally very weak in the Raman effect unless in Fermi resonance with a fundamental, it was more reasonable to assign the 1388 cm^{-1} Raman band as fundamental mode 14.

The in-plane CH deformation corresponding to benzene mode 3 was assigned by Evans (26) to a band at 1290 cm^{-1}. Green (27) reassigned this mode to a band at 1310 cm^{-1}. Pinchas (29) disagreed with this assignment, adducing the 11 cm^{-1} shift of this band in the spectrum of ^{18}O-phenol. Mode 3 should be insensitive to this labeling. He did not propose an alternative assignment but suggested that this absorption is masked by the band at 1256 cm^{-1}. Wilson (30) reassigned this mode to the band at 1285 cm^{-1} in the Raman spectrum of phenol vapor.

In this investigation, modes 3 and 14 are assigned at 1380 and 1345 cm^{-1} in the vibrational spectra of phenol. From the initial potential energy distributions the calculated frequencies of 1359 and 1326 cm^{-1} can be assigned to modes 3 and 14, respectively. Following Wilson's (30) reasoning, the higher frequency vibration, mode 3, is assigned to the only Raman band in this region, at 1380 cm^{-1} (the corresponding IR band occurs at 1385 cm^{-1}). Mode 14 is assigned to the infrared band at 1345 cm^{-1}. These assignments are reinforced by the potential energy distributions calculated by the final force field. Also, for benzene, mode 14 appears at 1309 cm^{-1} in the IR spectrum and mode 3 arises at 1346 cm^{-1} in the Raman spectrum. This assignment is supported by the point mass and zeroth approximation calculations, neither of which show the frequencies of these two modes switching in terms of relative magnitude.

The band at 814 cm^{-1} occurs as a doublet with a band at 827 cm^{-1}. The band at 814 cm^{-1} was attributed to mode 12 and the 827 cm^{-1} band was ascribed by Evans (26) and Green (27,28) to the substituent insensitive out-of-plane CH deformation, 10b. Pinchas altered this assignment based on the spectra of ^{18}O-phenol. Pinchas assigned the band at 827 cm^{-1} to an x-sensitive out-of-plane CH deformation due to its shift to 841 cm^{-1} in ^{18}O-phenol. He retained the assessment of the 814 cm^{-1} band as the x-sensitive in-plane mode 12. Bist (31) assigned the band at 827 cm^{-1} to an x-sensitive in-plane deformation. Both bands in this doublet are strong in the Raman spectrum of phenol. And, as Wilson (30) pointed out, both are strongly polarized in the Raman effect, so they both belong to the totally symmetric symmetry species, A', i.e., both are due to in-plane vibrations. Wilson proposed that the line at 827 cm^{-1} is due to mode 12 in resonance with the first overtone of mode 16a at a frequency of 817 cm^{-1}. He did not reassign the out-of-plane deformation, but suggested that it may also fall in this region. Based on UV studies, Bist (31) assigned this out-of-plane mode at 817 cm^{-1}.

In this investigation, mode 10a is assigned at 818 cm^{-1}. The bands at 814 and 827 cm^{-1} have low depolarization ratios (0.1,0.1) indicating that they are both due to in-plane modes. Initial calculations and initial refinements (excluding the frequency of vibration 10a) found the frequency attributed to this vibration to arise in the range 810 ± 40 cm^{-1}. Using the force field that resulted from a substituent refinement followed by a phenyl refinement, which usually gives the best fit, this band is calculated to arise at 814 cm^{-1}. Based on these calculations, on Bist's assignment of the vibration to 817 cm^{-1} in the UV spectrum (31), on the Raman spectrum of the powdered solid (which shows a triplet in this region, Fig. 11) and on the Raman spectrum of the liquid

recorded with the analyzer perpendicular to the polarization of the incident beam (Fig. 12), vibration 10a is assigned at 818 cm^{-1}.

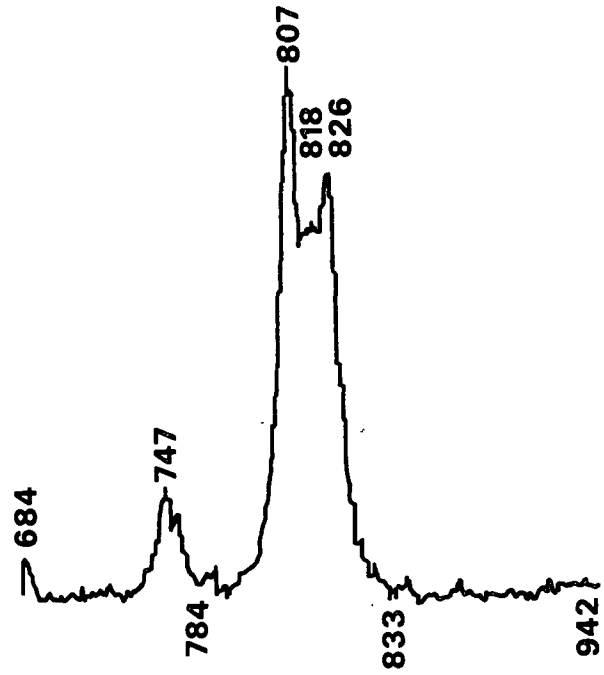


Figure 11. Portion of the Raman spectrum of a powdered sample of phenol, note bands at 807, 818, and 826 cm^{-1}.

The phenol modes derived from the in-phase and out-of-phase breathing modes, modes 1 and 12, have been assigned to bands at 999 cm^{-1} and 812 cm^{-1} (or 824 cm^{-1}), respectively by most authors (26,27,30,31) without comment. In his review of the behavior of the normal modes of benzene on substitution of the aromatic ring, Varsanyi (6) identified two intervals for mode 1, and one interval for mode 12 in monosubstituted benzenes. For heavy substituents (>25 amu) vibration 1 arises between 1060 and 1100 cm^{-1}. For light substituents it appears between 620 and 830 cm^{-1}. Vibration 12 occurs between 990 and 1010 cm^{-1}. Based on these observations and on the calculations performed in this investigation, the assignments of modes 1 and 12 are reversed. Mode 1 is assigned to the 812 cm^{-1} band and mode 12 is attributed to the 999 cm^{-1} band.

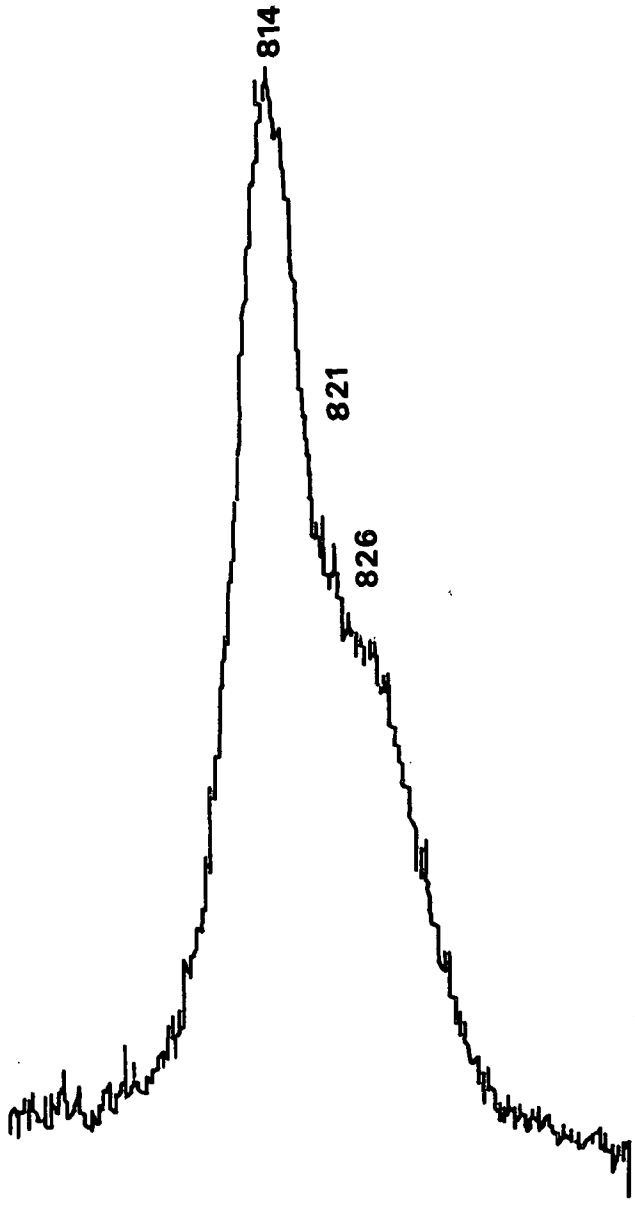


Figure 12. Raman spectrum of liquid phenol from 780 cm^{-1} to 860 cm^{-1} with the scattered light measured perpendicular to the polarization of the incident light at a resolution of one wavenumber.

The hydroxyl group gives rise to three fundamental modes in the spectra of phenol: the OH stretching mode, the torsion about the C-OH bond, and the COH in-plane bending mode. There is little controversy over the assignments of the

OH stretching and torsional modes, both having been studied exhaustively. The OH stretch of a free hydroxyl group gives rise to a sharp absorption near 3615 cm^{-1}. In a hydrogen bonded hydroxyl group this stretch generates a broad absorption band centered near 3330 cm^{-1} (78). The absorption of the torsion of a free hydroxyl group occurs at 310 cm^{-1}. In intermolecularly hydrogen bonded hydroxyl groups this mode becomes an OH out-of-plane bending vibration and appears at frequencies up to 700 cm^{-1}. In this investigation the free hydroxyl OH stretch and torsion are assigned to bands at 3602 and 309 cm^{-1}.

The assignment of the COH in-plane bending mode is not as straightforward. Evans (26) found that on change of the degree of association and on deuteration, two bands in the 1150-1400 cm^{-1} region behaved as expected for the OH bending mode: the band at 1344 cm^{-1} and that at 1180 cm^{-1}. Green (27) initially assigned this mode solely to the band at 1180 cm^{-1}, but later (28) admitted some contribution of this mode to the band at 1344 cm^{-1}. Pinchas (29) concurred with the assignment of these two bands: the shift of these bands in the spectra of ^{18}O-phenol was not as great as would be expected of a pure COH bending mode. The general consensus is that the band at 1180 cm^{-1} is due to COH in-plane bending with some ring stretching character and the band at 1344 cm^{-1} is due to a ring stretching vibration with some contribution from the COH deformation. However, coupling with a CCH bending fundamental (mode 3) has never been ruled out (26).

The assignment of the 1180 cm^{-1} band as the COH bending mode was accepted and used as a criterion for evaluating the potential energy distribution calculated by the final force field. This potential energy distribution showed the COH bend contributing to the band arising at 1380 cm^{-1} assigned as mode 3 and to

the band which occurs at 1345 cm^{-1}, ascribed to mode 14 in agreement with Pinchas, et al., (29).

Benzaldehyde

In a review of the assignments of the normal modes of benzaldehyde that have been published, several modes are noted to have differing assignments. The assignments of modes 19a, 19b, 18a, 18b, 14, 3, 6a, 9b and 10b, the in-plane aldehyde CH stretch and the out-of-plane wag of the aldehyde hydrogen vary. The assignments for these modes and for the other fundamental modes of benzaldehyde are listed in Table XXVIII.

Garrigou-Lagrange, et al., (36) assigned vibrations 19a and 19b to bands at 1490 and 1450 cm^{-1}. They assigned vibrations 18a and 18b to bands at 1023 and 1070 cm^{-1}. Degenerate modes 19 and 18 occur at 1478 and 1038 cm^{-1} in benzene and are noted to be insensitive to monosubstitution. Based on normal coordinate calculations of chlorobenzenes performed by Scherer (79,11), Zwarich, et al., (37) reversed these assignments. They attributed the bands at 1490 and 1450 cm^{-1} to modes 18a and 18b and those at 1023 and 1070 cm^{-1} to modes 19a and 19b. Green's (38) assignment of these bands concurred with the Garrigou-Lagrange assignment. The band at 1490 cm^{-1} was noted to be weak relative to its intensity in other monosubstituted benzene derivatives (36,38).

The calculations carried out in this investigation support the Garrigou-Lagrange (36) assignments, with modes 19a, 19b, 18a and 18b attributed to bands at 1496, 1458, 1023 and 1072 cm^{-1}, respectively. It is possible that Zwarich used the Duinker and Mills' numbering system for the benzene modes. This system is the same as Wilson's, save for an interchange of the numbers of modes 18 and 19.

TABLE XXVIII

ASSIGNMENTS OF THE NORMAL MODES OF BENZALDEHYDE

Infrared, cm^{-1}	Raman, cm^{-1}	Assignment
	128 m[a]	A" CHO torsion
	223 w	9b A' CX bend
	237 w	16b A" ring deformation
410 w		16a A" ring deformation
435 w	438 m	6a A' ring deformation
448 w	451 w	10b A" CX bend
615 mw	614 m	6b A' ring deformation
650 s	649 m	A' CCO bend
689 s		4 A" ring deformation
746 s	746 w	11 A" wag
828 s	827 m	1 A' ring deformation
	851 w	10a A" wag
924 w		17b A" wag
	969 vw	17a A" wag
	989 w	5 A" wag
1001 m	1000 vs	12 A' ring deformation
1008 w		A" H-CO wag
1023 m	1022 m	18a A' CCH bend
1072 m	1072 w	18b A' CCH bend
	1160 sh	15 A' CCH bend
1167 ms	1166 m	9a A' CCH bend
1204 s	1202 s	13 A' CX stretch
1288 m		14 A' CC stretch
1311 ms	1311 w	3 A' CCH bend
1391 m	1390 w	A' HCO bend
1456 ms	1455 w	19b A' CC stretch
	1490 w	19a A' CC stretch
1584 ms	1584 sh	8a A' CC stretch
1597 s	1596 s	8b A' CC stretch
1703 vs	1696 s	A' C=O stretch
2737 m	2737 m	A' H-CO stretch
3026 w		7a A' CH stretch
3031 w		20b A' CH stretch
	3046 sh	20a A' CH stretch
3064 m	3063 m	7b A' CH stretch
3086 w		2 A' CH stretch

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

Modes 3 and 14 arise at 1348 and 1309 cm^{-1} in the vibrational spectra of benzene. In benzaldehyde these modes were assigned to bands at 1292 and 1310 cm^{-1} by Green (38) and to bands at 1308 and 1292 cm^{-1} by Zwarich (37). Garrigou-Lagrange (36) assigned mode 3 at 1308 cm^{-1} but did not assign mode 14.

The potential energy distributions, calculated using the final force field for benzaldehyde, show the calculated wavenumbers, 1319 and 1286 cm^{-1} to correspond to phenyl modes 3 and 14, respectively. Therefore these modes are assigned to the experimental frequencies 1314 and 1288 cm^{-1}. This assignment parallels the assignment of these vibrations in phenol.

The in-plane and out-of-plane CCX bends, modes 9b(15) and 10b are expected to occur at low frequencies. These modes were assigned to bands at 240 cm^{-1} and 224 cm^{-1} in the IR spectrum of benzaldehyde (38,40,41,42). It is admitted that the in-plane mode is not distinguished from the out-of-plane mode with any certainty (38). These bands have depolarization ratios of 0.7 and 0.6, respectively, which suggest that the assignments should be reversed. Based on their normal coordinate calculations, Zwarich, et al., (37), did reverse these assignments. Their calculations indicated that the out-of-plane CX wag should be more sensitive to deuteration at the 1-position than the in-plane CX bend, shifting to a frequency about 30 cm^{-1} lower. This predicted behavior was observed for the band at 240 cm^{-1} upon deuteration of the 1-position, while the band at 224 cm^{-1} was shifted only slightly.

In this investigation, mode 10b is assigned at 240 cm^{-1} and mode 9b is assigned at 224 cm^{-1}. This assignment was based on the depolarization ratios of these two bands and on the potential energy distributions for these frequencies. This assignment is in agreement with Zwarich's assignment of these two bands.

Vibration 6a has been assigned to bands at 650 cm^{-1} (37) and 437 cm^{-1} (38). The 650 cm^{-1} band has also been assigned as the in-plane CC=O bend coupled to an in-plane ring mode (38,48). Based on the potential energy distributions calculated for these modes in this study, mode 6a is assigned to the band at 439

cm^{-1}. The 650 cm^{-1} band is assigned as an in-plane CC=O bend coupled with an in-plane ring mode.

The fundamental modes of the formyl group of benzaldehyde comprise four in-plane modes: the aldehyde C=O and CH stretches and the CCH and CC=O bends, and two out-of-plane modes: the aldehyde CH wag and the torsion about the C-CHO bond.

The carbonyl stretching frequency is one of the most characteristic bond frequencies of organic structures. The relatively constant frequency of this vibration in organic compounds implies an almost pure carbon-oxygen stretching mode. However, normal coordinate calculations have shown that there is considerable mixing of this stretch with other modes (37,67). The small variations of this mode have been ascribed partly to variations in the carbonyl stretching force constant and partly to differences in vibrational coupling to the rest of the molecule (80,43). In this investigation the C=O stretching vibration is assigned to the intense IR absorption at 1703 cm^{-1} and at 1696 cm^{-1} in the Raman spectrum.

The formyl CH stretching mode is expected to arise between 2600 and 2900 cm^{-1}. Two bands characteristic of aldehydes are observed in this region: at 2720 cm^{-1} and 2820 cm^{-1}. It is thought that this doublet results from a Fermi resonance interaction between the formyl CH stretching fundamental at 2720 cm^{-1} and the first overtone of the formyl CH bending vibration at 2820 cm^{-1} (44,45,46). The formyl CH bending vibration was assigned to a medium intense band in the IR spectrum at 1394 cm^{-1} (36,37,38,45). Green (38), however, cited a number of combinations that can account for these bands: 2851, 2817: 2 x 1387; 1387 + 1456; 2740: 1308 + 1456; 2697: 1308 + 1387. Green arbitrarily assigned the band at 2820 cm^{-1} as the fundamental. Zwarich (37) also assigned the fundamental to this frequency.

In this investigation the formyl CH stretching mode is assigned to the band at 2737 cm^{-1} in agreement with Saier (44), Eggers (45) and Pinchas (46). Though this assignment and the alternate assignment (to the band at 2820 cm^{-1}) both provide adequate solutions, the 2737 cm^{-1} assignment results in a better fit of the calculated to the observed frequencies.

Green (38) suggested that the in-plane C=O bend is coupled with the in-plane breathing mode of the aromatic ring. It was assigned to a band at 649 cm^{-1}. Garrigou-Lagrange (36) made the same assignment. Based on the potential energy distribution, a similar assignment is made in this study. The in-plane C=O bend is assigned at 649 cm^{-1}. This mode is coupled with an in-plane ring deformation.

Of the two out-of-plane vibrations of the formyl group, only the torsion has been assigned unambiguously. A band at 127 cm^{-1} in the spectrum of the liquid was attributed to this mode (40,41,47). It is assigned at 128 cm^{-1} in this investigation.

The out-of-plane wag of the formyl hydrogen was variously assigned to bands at 649 cm^{-1} (39), 826 cm^{-1} (36), and 1010 cm^{-1} (37,38). In their simplified normal coordinate calculations, Puranik and Rao (39) used the value 649 cm^{-1} for this mode. Garrigou-Lagrange (36) assigned the strong IR band at 826 cm^{-1} to this hydrogen wag despite the low depolarization ratio (0.06) of the corresponding Raman line. Because of this low depolarization ratio this assignment was rejected by Zwarich (37). Green (38) adduced the IR band contour of type A (characteristic of planar vibrations) as well as the low depolarization ratio in his rejection of this assignment. Using normal coordinate calculations, Zwarich calculated bands occurring at 978 and 1010 cm^{-1} with appropriate potential

energy distributions for this vibration coupled to benzene mode 5. Based on these calculations he assigned the CH out-of-plane wag to the 1010 cm^{-1} band. Green (38) concurred with Zwarich's assignment.

As it was unknown, the frequency of the formyl CH out-of-plane wag was excluded from the initial refinements of the out-of-plane force field. Using the initial force field and the results of the initial refinements, this band was calculated to arise at ca. 890 cm^{-1} for one set of initial force constants or at ca. 1000 cm^{-1} for the other initial set of force constants. Based on these normal coordinate calculations, the IR spectrum (there is a weak IR band at 1008 cm^{-1} but none near 890 cm^{-1}), and the observations of Zwarich (37) and Green(38) the out-of-plane hydrogen wag is assigned at 1008 cm^{-1} in this investigation.

Anisole

As in phenol and benzaldehyde, the fundamental modes of anisole have been unanimously assigned with a few exceptions. The assignments of phenyl modes 1, 12, 16b, 17b, 11, 10b, and 9b vary. Additionally, the antisymmetric CH stretching modes, the O-CH_3 stretch, the symmetric deformation of the CH_3 group, the rocking motions of the CH_3 group and the in-plane COC bend are not consistently assigned. The assignments proposed in this investigation for the normal modes of anisole are listed in Table XXIX.

Stephenson (52) attributed the band at 782 cm^{-1} to the in-phase breathing mode, mode 1, and the band at 994 cm^{-1} to the out-of-phase breathing mode, mode 12. Owen (50) gave the same assignment. Green reversed this assignment. Based on the potential energy distribution for anisole and Varsanyi's observations for monosubstituted benzenes (mode 1 should occur in the range 620-830 cm^{-1} and mode

TABLE XXIX

ASSIGNMENT OF THE NORMAL MODES OF ANISOLE

Infrared, cm^{-1}	Raman, cm^{-1}	Assignment
	(108)[a]	A" C-OCH_3 torsion
	214 m	16b A" ring deformation
	266 m	9b A' CCX bend
	(285)	A" O-CH_3 torsion
414 vw	416 vw	16a A" ring deformation
459 vw	443 s	6a A' ring deformation
514 w	513 w	10b A" CCX bend
554 w	553 w	A' COC bend
614 vw	614 s	6b A' ring deformation
692 s	695 vw	4 A" ring deformation
756 s	757 w	11 A" CCH bend
784 m	784 vs	1 A' ring deformation
820 vw	820 w	10a A" CCH bend
884 m	885 vw	17b A" CCH bend
960 vw		17a A" CCH bend
	975 m	5 A" CCH bend
995 w	995 vvs	12 A' ring deformation
1021 m	1021 s	18a A' CCH bend
1041 s	1039 s	A' O-CH stretch
1078 m	1078 w	18b A' CCH bend
1110 vw	1112 vw	A' methyl rock
1153 w	1153 m	A" methyl rock
1173 m	1172 s	15 A' CCH bend
1181 m	1181 s	9a A' CCH bend
1249 vs	1247 s	13 A' CX stretch
1303 m	1302 m	14 A' ring deformation
1336 w	1336 w	3 A' CCH bend
1442 m	1441 m	A' sym HCH bend
1442 m	1441 m	A" asym HCH bend
1454 m	1455 m	19b A' ring deformation
1468 m	1468 w	A' asym HCH bend
1498 s	1497 w	19a A' ring deformation
1588 m	1587 s	8a A' ring deformation
1601 s	1600 s	8b A' ring deformation
2836 m	2836 s	A' sym CH stretch
2945 m	2945 m	A' asym CH stretch
2957 m	2956 w	A" asym CH stretch
3033 w		7a A' CH stretch
	3037 sh	20b A' CH stretch
	3055 s	20a A' CH stretch
3063 w	3069 s	7b A' CH stretch
3093 w		2 A' CH stretch

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

12 in the range 990-1010 cm^{-1}) (6), vibration 1 is assigned in this investigation to a band at 784 cm^{-1} and the band at 995 cm^{-1} is attributed to vibration 12. This assignment agrees with those proposed by Stephenson (52) and Owen (50).

The assignments of vibrations 16b, 17b, 11 and 10b differ. The bands arising at 210, 510, 755 and 887 cm^{-1} were respectively ascribed to modes 16b, 17b, 11 and 10b by Stephenson, and to modes 11, 16b, 10b, and 17b, by Green. In this study, modes 16b, 10b, 11 and 17b are assigned to the bands at 214, 513, 757 and 885 cm^{-1}, respectively. These assignments are based on the information available from the potential energy distributions of these frequencies. The assignments of vibrations 11 and 17b are in accord with the assignments cited for other monosubstituted benzenes, as reviewed by Varsanyi (6). The assignment of modes 16b and 10b, however, are reversed. The assignment of these four bands is based strictly on the potential energy distributions for these frequencies and follows from the potential energy distributions of the corresponding benzene modes.

The bands arising from the two CX bending modes have not been conclusively identified in previous assignments. Owen (50) assigned the in-plane deformation to a band at 264 cm^{-1}, and the out-of-plane deformation to a band at 508 cm^{-1}. Lebas (42) assigned these deformations to the bands occurring at 209 cm^{-1} and 555 cm^{-1}. Tylli (56) observed two low frequency bands at 209-216 cm^{-1} and 256-263 cm^{-1}. He assigned these bands to x-sensitive ring fundamentals. The former was ascribed to mode 16b, and the latter to mode 18b with which he described the in-plane CX bend. Green (51) cited two alternative assignments for the out-of-plane CX vibration, 510 and 554 cm^{-1}. The band at 510 cm^{-1} was taken as the fundamental and that at 554 cm^{-1} was interpreted as a binary combination borrowing intensity from the fundamental. Stephenson (52) assigned the

in-plane CX vibration at 258 cm^{-1} and the out-of-plane vibraton at 511 cm^{-1}. Campagnaro and Woods (57) measured the far IR and Raman spectra of several benzene derivatives and assigned the in-plane CX bend to a band at 263 cm^{-1} with a Raman depolarization ratio of 0.58. They assigned the out-of-plane deformation to a Raman line at 215 cm^{-1} with a depolarization ratio of 0.85.

In this investigation the potential energy distribution for anisole shows the CX in-plane bending mode contributing to the band at 266 cm^{-1}, and the CX out-of-plane deformation giving rise to the band at 513 cm^{-1}. This agrees with the assignment proposed by Stephenson, et al., (52). In this assignment the CX in-plane and out-of-plane bending vibrations are considered to correspond to benzene modes 9b and 10b.

The twelve fundamental modes of the methoxyl group comprise three CH stretching vibrations, the O-CH_3 stretch, three deformations of the HCH angles, two methyl rocking modes (deformation of the OCH angles), the COC angle bend, and two torsions. Of these, one CH stretch, one HCH angle deformation, one OCH angle deformation and the two torsions have A" symmetry. Though A' modes are symmetric by definition, one of the A' modes is referred to as an antisymmetric mode to distinguish it from the other A' mode. Antisymmetric in this case refers to the symmetry of the mode with respect to the symmetry of the methyl group, rather than to the symmetry of the molecule as a whole.

The A' and A" antisymmetric CH stretching modes have been assigned at 3004 and 2950 cm^{-1}, respectively (50,54). These two stretching modes have also been assigned to bands at 2946 and 2912 cm^{-1} (52). No strong absorption occurs at the expected position of the symmetric stretching vibration, 2880 cm^{-1}. It has been suggested (50) that this fundamental is in Fermi resonance with the first

overtone of the CH_3 symmetric deformation which would also fall near 2880 cm^{-1}. Of the two bands believed to be participating in this resonance, 2930 and 2835 cm^{-1}, the lower was assigned as the fundamental (50).

The $O-CH_3$ stretch has most frequently been assigned to a band at 1040 cm^{-1} (50,52,54,59). Green (51) reversed the earlier assignment of 1039 as a $O-CH_3$ stretch and 1176 cm^{-1} as a CH_3 rock and assigned the $O-CH_3$ stretch at 1176 cm^{-1}. Bogatyreva (54) calculated contributions of this stretch to bands at 1107, 1076 and 1044 cm^{-1}, and assigned this stretch to the band at 1107 cm^{-1}.

The deformation modes of the CH_3 group were calculated by Bogatyreva to give rise to bands at 1468, 1453 and 1441 cm^{-1}. Owen (50) assigned the symmetric and antisymmetric A' deformations at 1440 and 1452 cm^{-1} respectively, and the A" antisymmetric deformation at 1466 cm^{-1}. Green (51) and Stephenson (52) assigned the symmetric deformation to a band at ca. 1300 cm^{-1} (1304 and 1296 cm^{-1}).

Owen noted that the rocking motions of the CH_3 group often coupled with other modes and did not produce consistent group frequencies in the substituted anisoles studied. He assigned absorptions at 1170 ± 40 and 850 ± 40 cm^{-1} in substituted anisoles to the A" and A' rocking modes. In anisole the A" mode was assigned at 1157 cm^{-1}, and the A' mode was not observed. Green assigned the A' OCH deformation to the 1039 cm^{-1} band, and the A" mode as coincident with a phenyl fundamental at 1076 cm^{-1}.

To aid in the assignment of these methoxyl modes, normal coordinate calculations were performed for methanol. The geometry, internal coordinates and force constants for methanol used by Wells (81), were used to calculate the normal frequencies of methanol. The mass of the hydroxyl hydrogen was then changed

to 77 amu (corresponding to the mass of a phenyl group) and the calculations repeated. In these calculations the frequencies of the CH stretching and OCH and HCH bending deformations were unchanged except for one of the OCH bending modes.

Based on this calculation, on the depolarization ratios of the Raman bands, and on the potential energy distributions of the various bands, the following assignments are made. The A' and A" antisymmetric CH stretching modes are assigned to bands at 2945 and 2957 cm^{-1}. The 1441 and 1468 cm^{-1} bands are attributed to the A' deformations of the CH_3 group, and a band at 1456 cm^{-1} is assigned as the A" deformation of this group. The A' rocking mode of the OCH_3 group is assigned to the band at 1112 cm^{-1} and the A" rocking mode is appointed to the band at 1154 cm^{-1}.

There has been no consistent assignment for the in-plane COC bend. It has variously been assigned at 352 cm^{-1} (51), 413 cm^{-1} (57) and 390 or 556 cm^{-1} (52). Bogatyreva (54) calculated contributions of this mode to bands at 258, 445 and 509 cm^{-1}. In substituted anisoles, Owen (50) assigned this bend to absorptions at ca. 310 cm^{-1}, but did not assign this mode in anisole.

The potential energy distribution calculated for anisole in this investigation indicated that the bands at 266, 443 and 553 cm^{-1} are all due, in part, to the COC in-plane bend. The largest contribution from this mode is to the 553 cm^{-1} band which is assigned as the in-plane COC bend.

The torsional vibration of a methyl group is usually a very weak absorber in the infrared (50). Though no band was observed for this mode, Owen proposed its position to be 220 ± 30 cm^{-1} by analogy to methyl vinyl ether. Tylli (56) did not observe this torsional band in the vibrational spectrum of liquid anisole,

either. However, in solid anisole a band appeared at 285 cm^{-1} which he attributed to this torsion. The second torsional mode, about the C-OCH_3 bond, has been assigned in the 108-115 cm^{-1} range (50,56,57).

In this investigation, the torsion about the O-CH_3 bond is calculated to occur at 110 cm^{-1}. The C-OCH_3 torsion is calculated to occur at 290 cm^{-1}. These bands are not observed in the vibrational spectra recorded in this study, so are not assigned.

Comparison of the Frequencies and Intensities of the Phenyl Modes

One of the focal points of this investigation is the effect the addition of a substituent to the benzene ring has on the frequencies and intensities of the benzene fundamental modes. It is therefore of interest to compare the assignments of the normal modes of the monosubstituted benzenes.

Frequency

Comparison of the frequencies of the phenyl modes in monosubstituted benzenes to these modes in benzene indicates that six phenyl modes are sensitive to monosubstitution. This can be seen in Table XXX which lists the observed frequencies of the fundamental modes of benzene and the phenyl modes of the monosubstituted benzenes. This is also obvious in line representations of the vibrational spectra of these compounds, as shown in Fig. 13. For the monosubstituted benzenes, modes undergoing shifts of less than 100 cm^{-1} on substitution are classified as substituent insensitive. The modes shifting more than 100 cm^{-1} are substituent sensitive. The shifts of substituent sensitive modes range from less than 200 cm^{-1}, as in modes 6a and 16b, to ca. 1800 cm^{-1}, as in mode 13. The modes associated with the CX bond undergo the largest shifts. Three of the x-sensitive modes are associated with the CX bond. They include

TABLE XXX

WAVENUMBERS (cm^{-1}) OF THE BENZENE MODES AND THE PHENYL MODES OF MONOSUBSTITUTED BENZENES

Mode	Benzene	Phenol	Benzaldehyde	Anisole
		In-plane Modes		
2	3064	3087	3088	3093
7b	3055	3076	3065	3069
20a	3055	3061	3045	3055
20b	3043	3046	3035	3037
8b	1594	1605	1600	1600
8a	1594	1595	1588	1587
19a	1483	1499	1496	1497
19b	1483	1471	1458	1455
3	1348	1388	1314	1336
14	1309	1345	1288	1304
13*	3037	1251	1205	1248
7a	3043	3022	3026	3033
15	1149	1152	1162	1172
9a	1179	1168	1168	1181
18b	1039	1071	1072	1078
18a	1039	1024	1023	1021
12	1012	999	1002	995
1*	999	812	830	784
6b	608	618	615	615
6a[a]	608	530	439	443
9b*	1179	413	230	266
		Out-of-Plane Modes		
5	990	986	989	975
17a	968	958	962	960
17b	968	890	924	885
10a	850	818	851	820
10b*	850	509	451	513
4	704	690	689	692
11	672	756	746	757
16a	404	416	410	415
16b*	404	242	237	214

*Substituent sensitive modes.

the CX stretch, mode 13, the in-plane CCX bend, mode 9b and the out-of-plane CCX bend, mode 10b. As would be expected, substitution on the ring has the greatest effect on these modes. The other three modes classified as x-sensitive in this study are modes 1, 6a and 16b. The potential energy distribution of these three

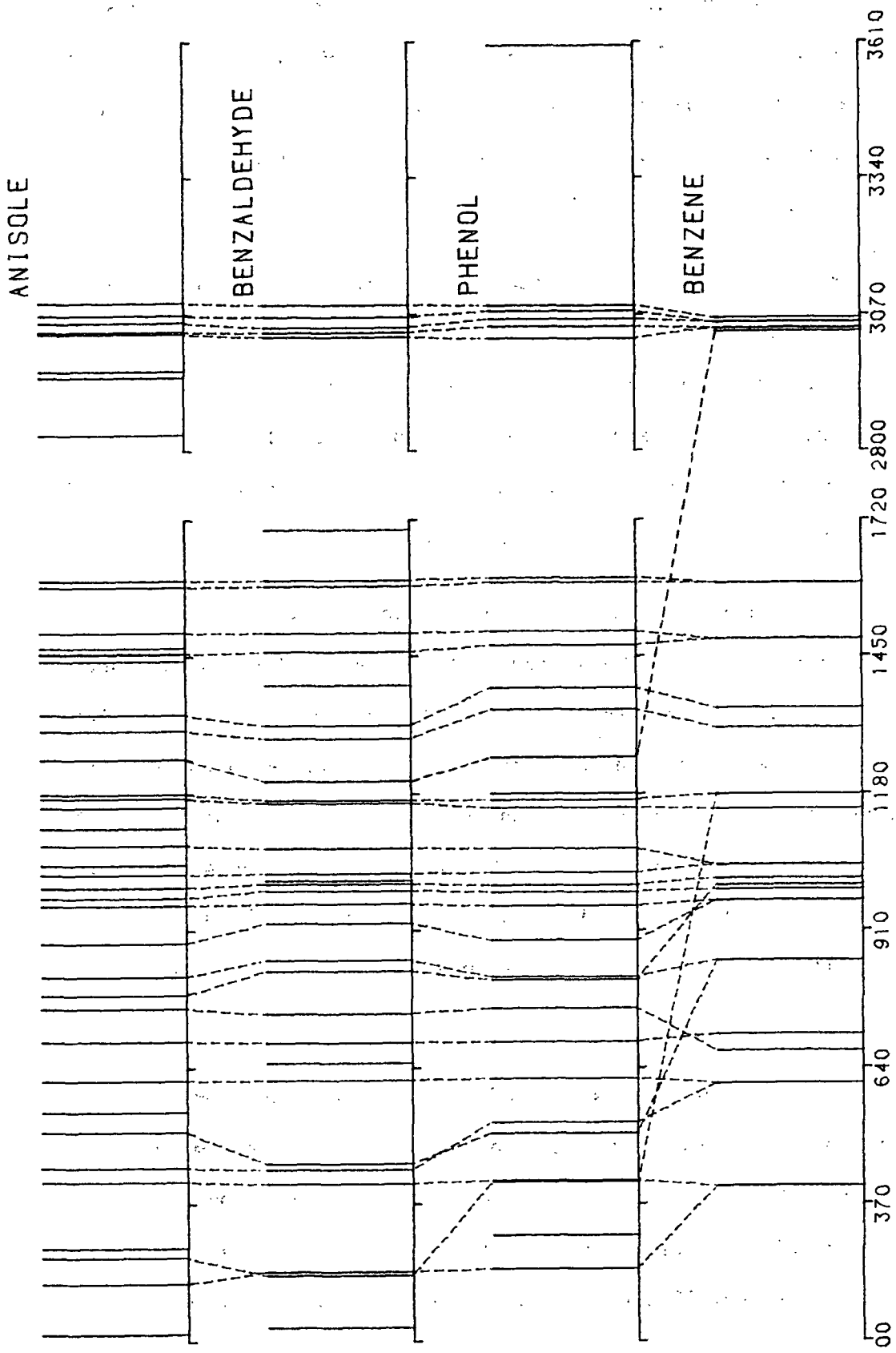


Figure 13. Comparison of the phenyl modes of monosubstituted benzenes. The dashed lines connect the phenyl modes.

modes show them to be substantially coupled with the motions of the CX bonds. These six modes were also identified to be x-sensitive by Whiffen (21). Varsanyi (6) classified mode 3 as x-sensitive and mode 16b as x-insensitive. The remaining modes are only slightly shifted on substitution and are considered to be substituent insensitive.

The effect of the chemical nature of the substituent on the normal modes of the ring can be seen in Fig. 13 as well. Anisole and phenol have electron-donating substituents. Benzaldehyde has an electron-withdrawing substituent. The effect of these differing chemical natures is seen as slight shifts to higher or lower frequencies in the spectrum of benzaldehyde as compared to the phenol and anisole spectra, as in modes 13, 17b, 10a and 10b.

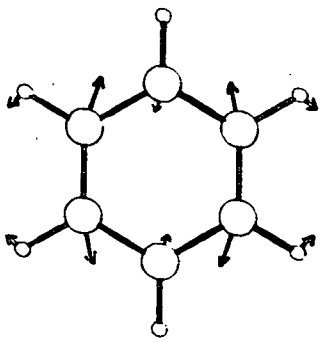
The influence of the mass of the substituent on the normal modes of the ring can also be seen in Fig. 13. The masses of the formyl and methoxyl groups are within 2 amu. The mass of the hydroxyl group is 12-14 amu lower. The effect of this difference in mass is seen in the behavior of some modes which shift in frequency in the spectrum of benzaldehyde relative to phenol and remain at that frequency in the spectrum of anisole. This behavior is seen in modes 6a and 9b. Combinations of these two effects (chemical nature and mass) can be seen in the slight frequency shifts of several of the other modes, e.g., modes 3 and 14.

Intensity

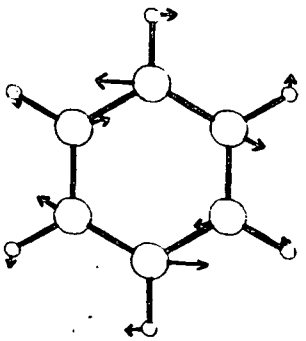
Comparisons of the relative intensities of the bands arising from the fundamental modes of the phenyl ring show the intensities of the phenyl modes to vary considerably from those of the benzene molecule, and to vary somewhat between the monosubstituted benzenes. The intensity of infrared bands is a function of the change in the overall dipole moment of the molecule. The changes in

the intensities of the IR bands can be interpreted using an analysis of the form of the vibration. For example, phenyl modes 8a and 8b are CC stretching modes, where opposite sides of the ring move apart and together in-phase (Fig. 14). In benzene, this mode produces no change in the overall dipole moment and is inactive in the IR. In monosubstituted benzenes there is a change of dipole moment with this vibration, so the band is IR active. The intensity of this IR band increases as the polarity of the substituent increases (82). Both modes 8a and 8b behave in this manner, though the lower frequency band (8a) is slightly weaker.

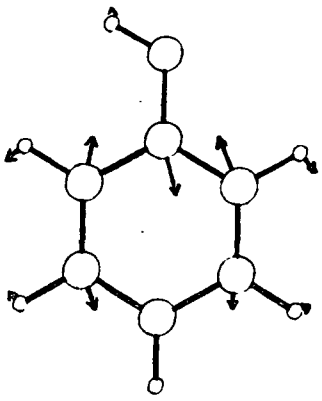
Normal Mode 8A = 1599 cm^{-1}



Normal Mode 8B = 1599 cm^{-1}



Normal Mode 8A = 1618 cm^{-1}



Normal Mode 8B = 1590 cm^{-1}

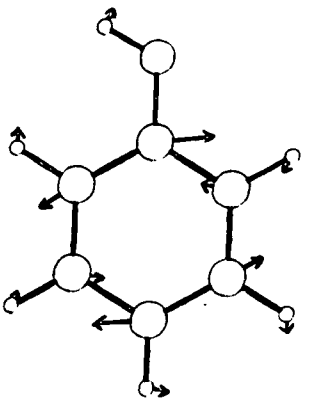


Figure 14. Modes 8a and 8b in benzene (top) and phenol (bottom).

The IR intensities of vibrations 8a and 8b have been found to give a measure of the electronic interaction between the substituent and the ring for monosubstituted benzenes. Katritzky (23,83) and Brownlee (84, 85,86) found relationships between the intensities of the two bands at 1600 cm^{-1} for monosubstituted benzenes and the resonance effects of the substituent. Brownlee (84,85,86) found that the intensities of these bands could be used to calculate the σ_R° for the substituents (σ_R° is the resonance contribution to the Hammett correlation coefficient σ_p°). Qualitatively, the same trend in the intensities of the 1600 cm^{-1} bands for phenol, benzaldehyde and anisole were observed in this study as that observed by Brownlee (he found the square roots of these intensities to be 54.2, 33.9, and 57.7 $l.mole^{-1}$ cm^{-2}, respectively).

Raman intensities depend on vibrational changes of the polarizability rather than on the dipole moment. And to some extent the changes in the intensities of the Raman bands can be explained based on the form of the vibration. However, Raman intensities of some bands can also be influenced by resonance Raman effects, and in substituted benzenes, by the amount of π-electron conjugation between the ring and the substituent (87-91,92). In the resonance Raman effect, the Raman intensity increases when the frequency of the exciting radiation approaches a frequency corresponding to an electronic transition. The resonance Raman effect has been noted to be nonuniform for different Raman lines of the same molecule (88). As well, only the intensities of certain bands are affected by conjugation effects. Schmid and Brosa also found that increasing the extent of conjugation by increasing the chain length of the diphenylpolyenes enhanced the intensity of the 1600 cm^{-1} bands but not that of the CH stretching bands (88).

In monosubstituted benzenes, the resonance Raman effect is thought to have little influence on the intensities of the two bands at 1600 cm^{-1}. However, the intensities of these bands are affected by conjugation effects (90). Schmid found the sum of the intensities of the bands of modes 8a and 8b to be 4.15, 0.77, and 1.06 for benzaldehyde, phenol and anisole, respectively (91). Qualitatively, the same trends are observed for the intensities of these bands in this investigation. None of the other bands in the Raman spectrum of monosubstituted benzenes have been noted to be as consistently influenced by conjugation effects.

As another example, degenerate mode 19 has a strong IR band and is inactive in the Raman spectrum of benzene. Mode 19 is a CC stretching mode in which the opposite sides of the ring are moving in the same direction (Fig. 15). The dipole-moment change created by this vibration is little affected by monosubstitution. This band occurs with strong to medium intensity in the IR, and with weak intensity in the Raman.

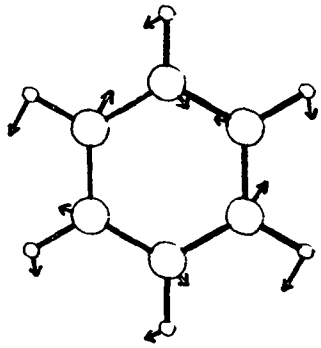
The forms of the fundamental modes of phenol are shown in Fig. 16. In these diagrams the lengths of the arrows are proportional to the extent of the displacement of that atom in the vibration. Comparison of these diagrams with those given for benzene (Fig. 2) along with knowledge of the chemical nature of the substituents can explain most of the intensity variations.

SUMMARY

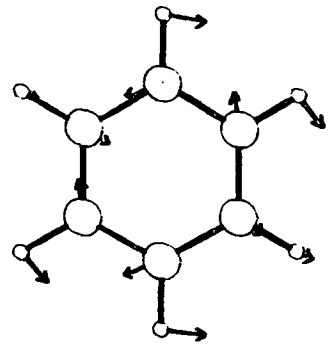
Modified valence force fields were developed for phenol, benzaldehyde, and anisole. The MVFF's were constructed from the phenyl force field developed in Chapter I and appropriate substituent force fields. Results of calculations using these initial force fields and group frequency data were used to initially assign the spectra. Force constants to account for interactions between the

substituent and the ring were added to the initial force field. The force field was then refined to minimize the difference between the observed and calculated frequencies. The final refined force fields had reasonably valued force constants. The potential energy distribution calculated using these was reasonable, and the observed frequencies were accurately calculated. Using the results of these calculations, the assignments of the vibrational spectra of the monosubstituted benzenes were completed. The assignments of these spectra were compared to determine the effect of monosubstitution of the aromatic ring on the frequencies and intensities of the fundamental modes of benzene.

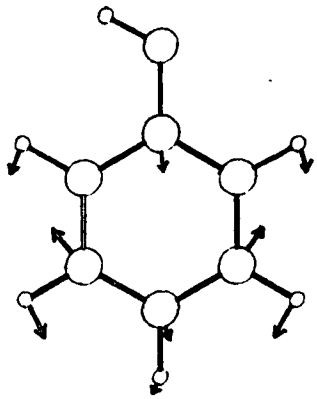
Normal Mode 19A = 1482 cm^{-1}



Normal Mode 19B = 1482 cm^{-1}



Normal Mode 19B = 1462 cm^{-1}



Normal Mode 19A = 1500 cm^{-1}

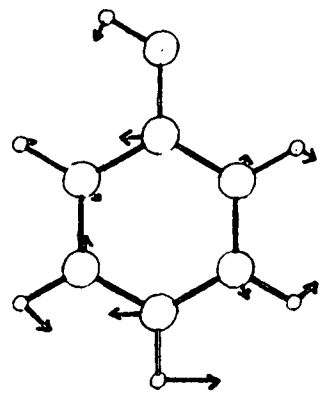
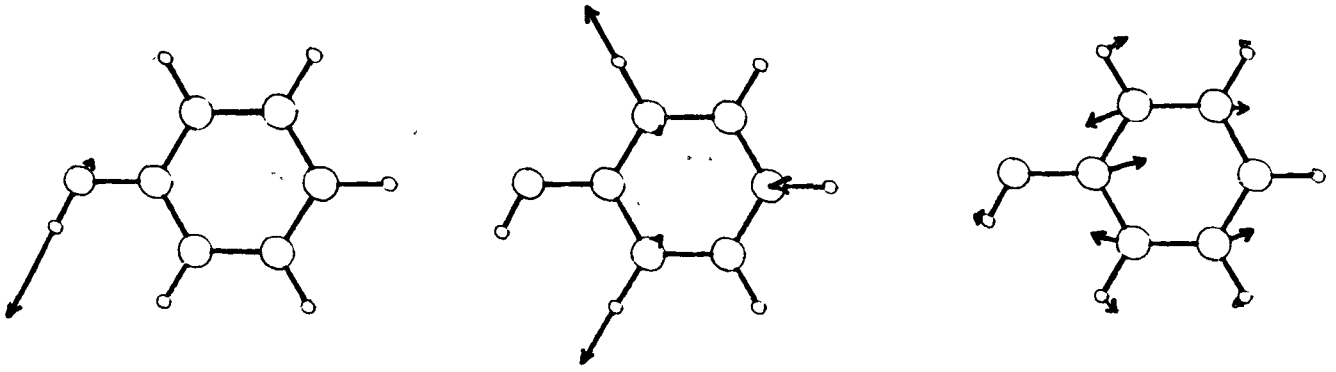
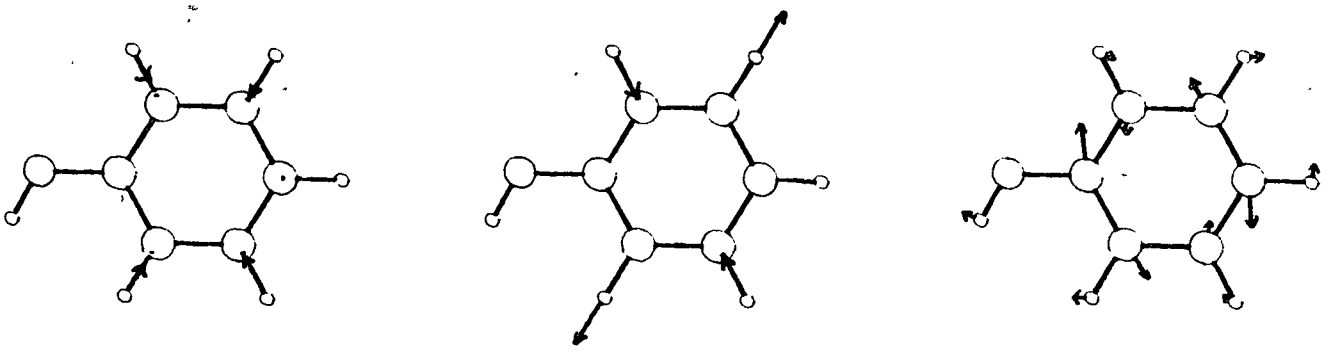


Figure 15. Modes 19a and 19b in benzene (top) and phenol (bottom).

Normal Mode OH = 3609 cm^{-1} Normal Mode 20A = 3056 cm^{-1} Normal Mode 8A = 1618 cm^{-1}



Normal Mode 2 = 3087 cm^{-1} Normal Mode 7A = 3038 cm^{-1} Normal Mode 8B = 1590 cm^{-1}



Normal Mode 20B = 3072 cm^{-1} Normal Mode 7B = 3028 cm^{-1} Normal Mode 19A = 1500 cm^{-1}

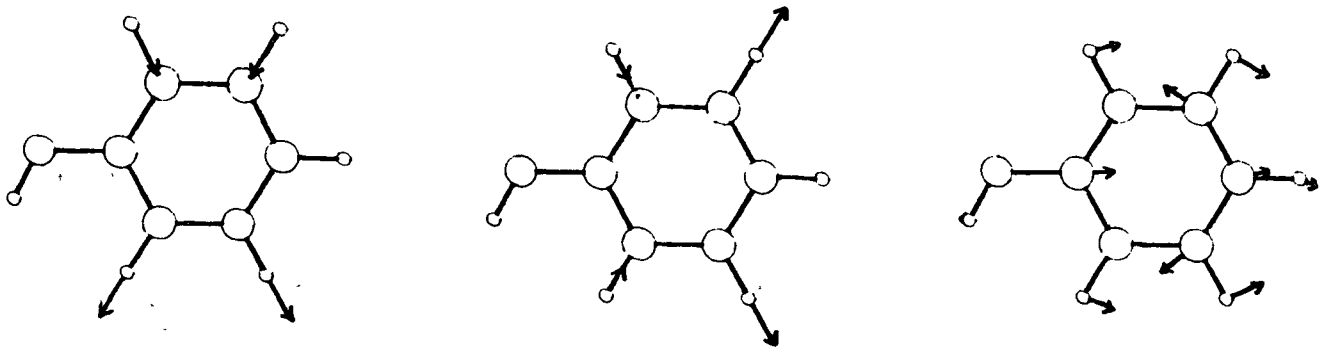
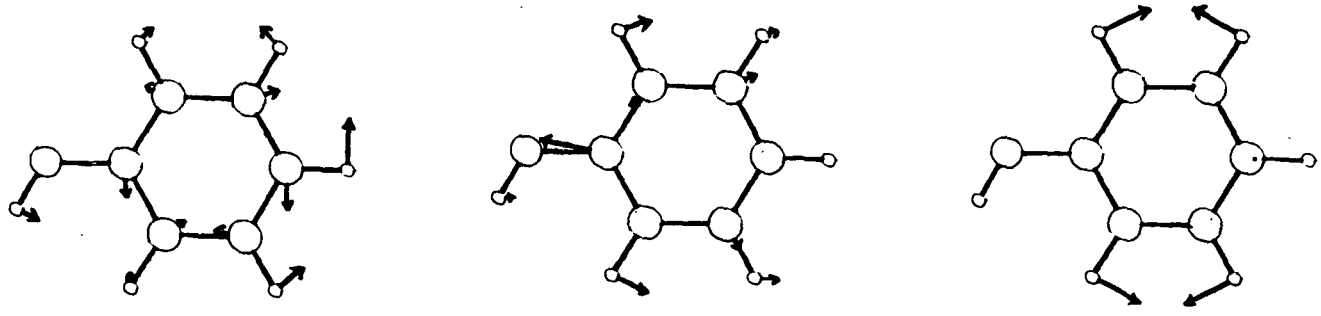
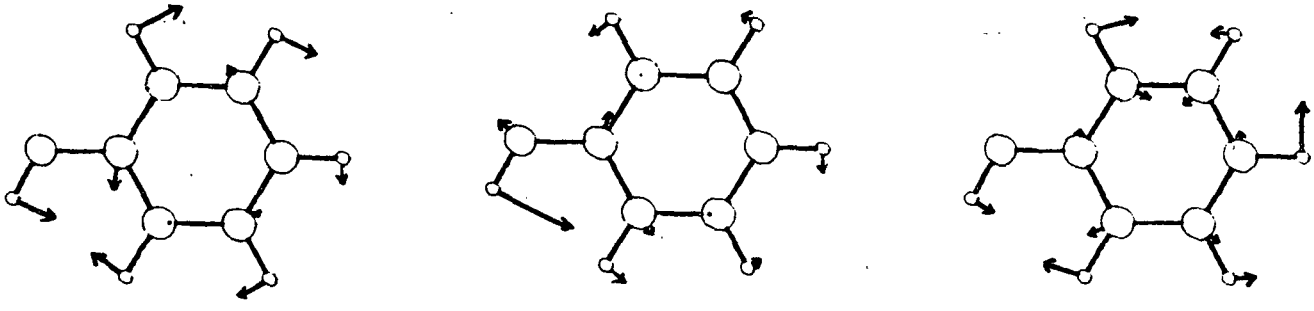


Figure 16a. The in-plane vibrations of phenol.

Normal Mode 19B = 1462 cm^{-1} Normal Mode 13 = 1266 cm^{-1} Normal Mode 9A = 1162 cm^{-1}



Normal Mode 3 = 1361 cm^{-1} Normal Mode COH = 1181 cm^{-1} Normal Mode 18A = 1071 cm^{-1}



Normal Mode 14 = 1324 cm-1 Normal Mode 15 = 1170 cm-1 Normal Mode 18B = 1019 cm-1

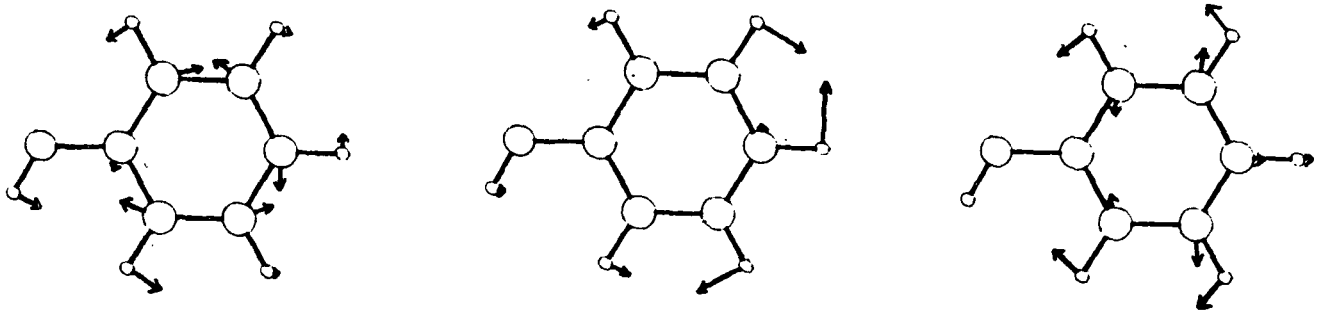
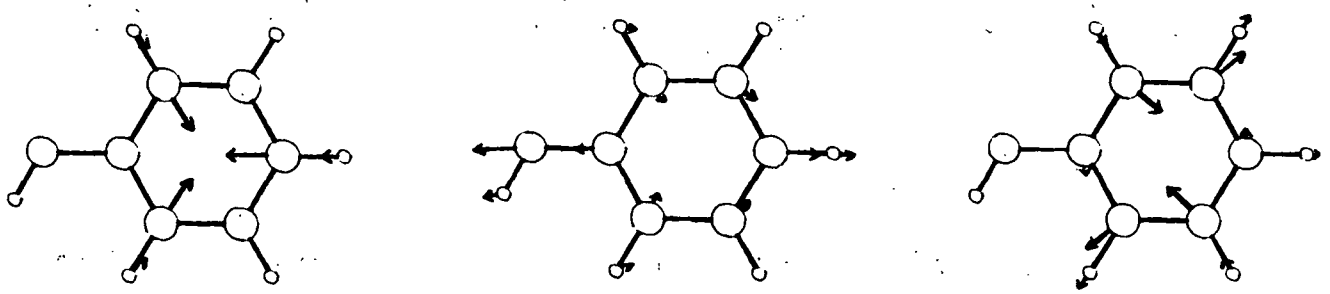


Figure 16a (Continued). The in-plane vibrations of phenol.

Normal Mode 12 = 997 cm^{-1} Normal Mode 6B = 504 cm^{-1} Normal Mode 6A = 617 cm^{-1}



Normal Mode 1 = 807 cm^{-1} Normal Mode 9B = 419 cm^{-1}

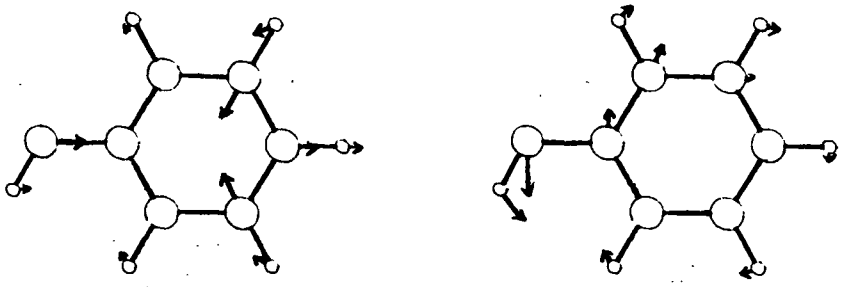
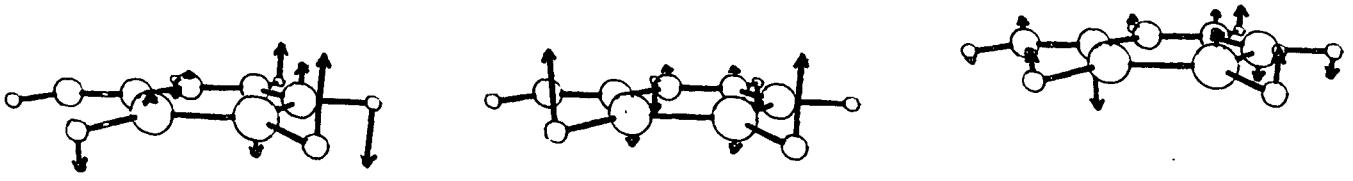
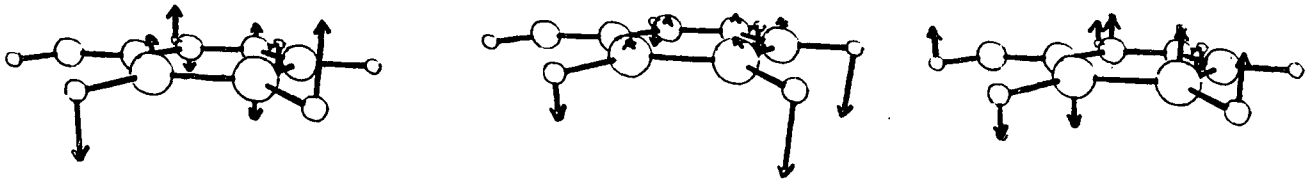


Figure 16a (Continued). The in-plane vibrations of phenol.

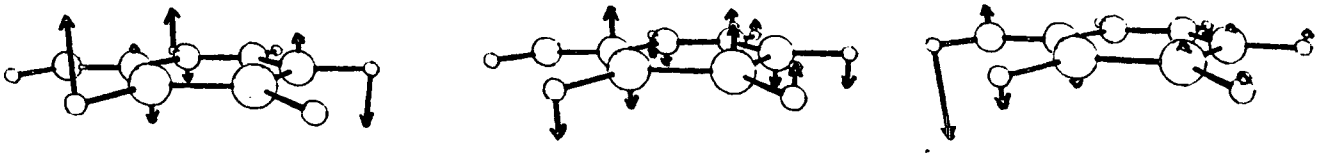
Normal Mode 5 = 986 cm^{-1} Normal Mode 10A = 829 cm^{-1} Normal Mode 10B = 514 cm^{-1}



Normal Mode 17A = 960 cm^{-1} Normal Mode 11 = 756 cm^{-1} Normal Mode 16A = 416 cm^{-1}



Normal Mode 17B = 904 cm^{-1} Normal Mode 4 = 687 cm^{-1} Normal Mode CCOH = 308 cm^{-1}



Normal Mode 16B = 240 cm^{-1}

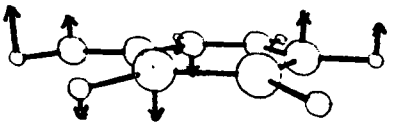


Figure 16b. The out-of-plane vibrations of phenol.

The majority of the assignments proposed for the monosubstituted benzenes agree with published assignments. However, different assignments were suggested for several of the fundamental modes of these compounds. Comparison of these assignments identified the frequencies of six of the benzene modes to be substituent sensitive. Three of these modes are associated with the CX bond, two are in-plane ring deformations, and one is an out-of-plane ring deformation. These substituent sensitive modes were found to be primarily sensitive to the fact that the ring had been substituted, and were slightly influenced by the nature or mass of the substituent. The intensities of the phenyl bands were more sensitive to substitution than were the frequencies. The intensities are influenced by both the nature of the substituent and the form of the mode.

CHAPTER III. ANALYSIS OF THE VIBRATIONAL SPECTRA OF THE DISUBSTITUTED BENZENES: 4-HYDROXYBENZALDEHYDE, GUAIACOL, m-ANISALDEHYDE

INTRODUCTION

The vibrational spectra of 4-hydroxybenzaldehyde, guaiacol, and m-anisaldehyde are assigned to ascertain the effect of disubstitution of the aromatic ring on the normal modes of benzene. The modified valence phenyl and substituent force fields developed for the monosubstituted benzenes in Chapter II are used to calculate the frequencies of the normal modes of the disubstituted benzenes. These frequencies and their potential energy distributions are used along with group frequency data and spectral information to assign the normal modes of the compounds. The assignments of these compounds will aid in the interpretation of the vibrational spectra of the trisubstituted benzene, vanillin, and of lignins.

The normal coordinate calculations and band assignments for the disubstituted benzenes are presented in this section. The literature on the assignment of the phenyl modes in the vibrational spectra of disubstituted benzenes in general and on the assignment of the spectra of 4-hydroxybenzaldehyde, guaiacol and m-anisaldehyde is briefly reviewed. The construction of the kinetic and potential energy matrices is discussed. The assignments of the IR and Raman spectra are presented. And, the behavior of the phenyl and substituent modes on disubstitution of the ring is discussed.

LITERATURE REVIEW

To aid in the interpretation of the vibrational spectra of 4-hydroxybenzaldehyde, guaiacol and m-anisaldehyde, the literature discussing the assignment of the fundamental phenyl modes in disubstituted benzenes is briefly reviewed.

Previous assignments of the spectra of these three disubstituted benzenes have been based primarily on group frequency information. These assignments are also mentioned, the details of which are reviewed in the discussion of the assignments proposed in this investigation.

VIBRATIONAL SPECTRA OF DISUBSTITUTED BENZENES

The symmetry of a disubstituted benzene is lower than that of benzene. When the substituents are identical, the symmetry of the molecule is C_{2v}. When the substituents differ, the molecular symmetry becomes C_S (except for a p-disubstituted benzene with two monatomic or linear substituents whose symmetry would be C_{2v}). Under the C_S point group, the thirty benzene fundamental vibrations divide into twenty-one A' and nine A" modes. The A' vibrations are in-plane modes, the A" vibrations are out-of-plane modes.

As in monosubstituted benzenes, the phenyl modes can be divided into substituent sensitive and substituent insensitive modes. The effect of disubstitution, however, is not as regular as that of monosubstitution. The number of substituent sensitive modes is known to increase with increasing substitution, but a unique number of x-sensitive modes in disubstituted benzenes has not been identified. The positions of the substituents relative to each other in addition to the mass and chemical nature of the substituents determine the frequencies of the phenyl modes.

Green (93-95), Bogomolov (96-98), Katritzky (99-101), Bellamy (82) and Varsanyi (6) discuss the effect of disubstitution of benzene on the fundamental modes of the ring. The observations presented in these papers, as they pertain to 4-hydroxybenzaldehyde, guaiacol, and m-anisaldehyde, are reviewed here.

The effect of disubstitution of benzene is discussed in more detail in Appendix II.

In disubstituted benzenes, two of the hydrogens are replaced with substituents. So two each of the six CH stretching, six CH in-plane bending, and six CH out-of-plane bending modes of the phenyl ring are x-sensitive. The other CH stretching, in-plane bending and out-of-plane bending modes of the phenyl ring are generally considered to be substituent insensitive. Varsanyi (6), however, considers the in-plane CH bend, mode 3, to be somewhat x-sensitive.

The two CX stretching modes, 7a and 13, are considered to be (6) sensitive to the masses of the substituents as well as the pattern of substitution. Based on the masses of the substituents, modes 7a and 13 are expected to occur in the ranges 150-400 cm^{-1} and 1100-1320 cm^{-1} in the p-disubstituted benzene, 4-hydroxybenzaldehyde. In the m-disubstituted benzene, m-anisaldehyde, modes 7a and 13 arise between 260 and 480 cm^{-1} and between 250 and 430 cm^{-1}, respectively. In guaiacol, an o-disubstituted benzene, the two CX stretching modes, 7a and 13, should occur in the ranges 250-500 cm^{-1} and 1080-1270 cm^{-1}.

The four CX bending modes are sensitive principally to the pattern of substitution on the ring. The two CX in-plane bending modes, 9b and 15, are expected to occur between 135 and 330 cm^{-1}, and between 250 and 450 cm^{-1}, respectively, in guaiacol. In m-anisaldehyde, modes 9b and 15 should arise in the ranges 170-360 cm^{-1} and 260-480 cm^{-1}. In 4-hydroxybenzaldehyde mode 9b should occur at 255-460 cm^{-1} and mode 15 at 190-350 cm^{-1}. The two CX out-of-plane modes, 10b and 11 are assigned to the ranges 125-196 cm^{-1} and 171-298 cm^{-1}, respectively, in guaiacol, the ranges 126-235 cm^{-1} and 196-271 cm^{-1} in m-anisaldehyde, and the ranges 240-380 cm^{-1} and 80-220 cm^{-1} in 4-hydroxybenzaldehyde.

All four in-plane ring deformations are substituent sensitive in o-disubstituted benzenes. These modes are sensitive to the masses of the substituents, heavy (>25 amu) or light (<25 amu). In guaiacol the in-phase breathing mode, mode 1, should occur between 1020 and 1070 cm^{-1}. The out-of-phase breathing mode, mode 12, should arise in the 750-860 cm^{-1} range. Mode 6a should be in the 640-720 cm^{-1} range. Mode 6b should occur below 560 cm^{-1}.

In m-disubstituted benzenes, only three of the in-plane ring deformations are substituent sensitive. Modes 1, 6a and 6b are all shifted, their frequency ranges dependent on the masses of the substituents. For m-anisaldehyde, modes 1, 6a and 6b should arise in the ranges 650-750, 450-550 and 700-900 cm^{-1}, respectively. The out-of-phase breathing mode (mode 12) is substituent insensitive in m-disubstituted benzenes.

In-plane ring deformational modes 1, 6a and 12 are considered to be substituent sensitive in p-disubstituted benzenes. Mode 6b is classified as x-insensitive. Again the frequency shifts of the x-sensitive modes are dependent on the masses of the substituents. For 4-hydroxybenzaldehyde modes 1, 6a and 12 should be in the ranges 1050-1100, 680-840 and 480-680 cm^{-1}.

The five CC stretching modes of the phenyl ring are all considered to be substituent insensitive in o- and m-disubstituted benzenes. Varsanyi (6) classified mode 14 as x-sensitive in p-disubstituted benzenes. The three out-of-plane ring deformations are substituent insensitive in benzene derivatives of all three disubstitution patterns. The frequency ranges for the phenyl modes of disubstituted benzenes are summarized in Table XXXI.

TABLE XXXI

WAVENUMBER (cm^{-1}) RANGES FOR DISUBSTITUTED BENZENES

	Ortho	Meta	Para
CH stretching modes			
2, 7a, 20a, 20b	3000-3120	3000-3120	3050-3090
CC stretching modes			
8a	1573-1581	1595-1575	1570-1628
8b	1600-1618	1600-1620	1552-1605
14	1250-1290	1300-1350	1330-1380
19a	1430-1470	1430-1467	1460-1530
19b	1450-1520	1471-1495	1370-1470
CH in-plane bending modes			
3	1252-1292	1262-1297	1260-1313
9a	1103-1148	1149-1166	1158-1182
18a	1150-1168	1061-1091	1004-1022
18b	1011-1056	1082-1109	1100-1128
In-plane ring deformations			
1 l,l[a]	630-780	650-750	720-860
1 h,h	1100-1130	1050-1140	1050-1100
6a l,l	560-600	450-550	330-480
6a h,h	640-720	640-710	680-840
6b l,l	< 560	350-520	623-650
6b h,h	650-750	700-900	623-650
12 l,l	750-860	990-1010	680-760
12 h,h	1010-1050	990-1010	1060-1100
CH out-of-plane bending modes			
5	978-987	950-990	920-970
10a	770-735	750-810	800-880
17b	932-949	860-900	800-880
17a	841-864	830-880	920-970
Out-of-plane ring deformations			
4	685-735	675-700	665-735
16a	480-530	460-600	ca 400
16b	410-470	400-490	410-550
CX modes			
9b CX in-plane bend	135-330	170-360	255-460
15 CX in-plane bend	250-450	260-480	190-350
7a CX stretch l,l	1120-1340	1120-1300	1100-1270
7a CX stretch h,h	250-500	260-480	150-400
13 CX stretch l,l	1080-1270	760-900	1100-1320
13 CX stretch h,h	1080-1270	250-430	360-550
10b CX out-of-plane bend	125-196	126-235	240-380
11 CX out-of-plane bend	171-298	196-271	80-220

[a]Light (l), < 25 amu; heavy (h), > 25 amu.

VIBRATIONAL SPECTRA OF THE MODEL COMPOUNDS

4-Hydroxybenzaldehyde

As phenol and benzaldehyde are planar, 4-hydroxybenzaldehyde is generally considered to be a planar molecule with C_S symmetry. Under this point group its thirty-nine fundamental frequencies divide into twenty-seven in-plane or A' modes and twelve out-of-plane or A" modes. All thirty-nine vibrations are both IR and Raman active. Discussions of portions of the vibrational spectrum of this p-disubstituted benzene derivative have been included in studies of hydrogen bonding, torsional barriers and p-disubstituted phenols. These spectra have been interpreted primarily by group frequency analysis. No normal coordinate studies of 4-hydroxybenzaldehyde have been found.

Assignments for the phenyl modes of 4-hydroxybenzaldehyde were proposed by Jakobsen and Brewer (102) and by Martin, et al., (103). Assignments for the fundamental modes of the formyl and hydroxyl group were proposed by Puttnam (104), Fateley, et al., (10), Aihara and Shirota (106), and Berthelot, et al., (107). The assignments of the phenyl modes that are assigned by both Jakobsen (102) and Martin (103) agree, with the exception of mode 12. Of the substituent modes, the in-plane COH bend, the C=O stretch and the C-CHO torsion have varying assignments.

Guaiacol

Guaiacol is the common name for o-methoxyphenol. This ortho-disubstituted benzene has forty-five fundamental modes. If the molecule has a plane of symmetry, which would make it a member of the C_S point group, these modes divide into thirty A' and fifteen A" modes. Most analyses of the vibrational spectra of guaiacol assume it to have a plane of symmetry coincident with the plane of

the ring. Portions of the vibrational spectra of guaiacol have been interpreted in studies of substituted phenols. Group frequency analysis has been the principal means of analyzing these spectra. Infrared vapor band contours, Raman depolarization ratios, and deuteration (of the hydroxyl group) studies have aided in these assignments.

Green, et al., (28), Verma, et al. (108) and Tripathi and Tripathi (109) all assign several of the phenyl modes of guaiacol. Overall, their assignments agree except for several of the substituent sensitive modes. The in-phase and out-of-phase ring breathing modes and the two CX stretching modes all have a variety of assignments. Opposing assignments also exist for the majority of the substituent modes.

m-Anisaldehyde

m-Anisaldehyde, or 3-methoxybenzaldehyde, is generally considered to belong to the C_S point group, with its plane of symmetry coincident with the plane of the aromatic ring. Under this point group, its forty-eight fundamental modes separate into thirty-two A' and sixteen A" modes. Twenty-one of the A' modes correspond to the in-plane modes of benzene. Nine of the A" modes are derived from the out-of-plane modes of the aromatic nucleus. The remaining fundamentals arise in the substituent groups. Motions of the formyl group give rise to three A' and two A" modes. The methoxyl group is responsible for twelve vibrations, seven A' and five A."

The vibrational spectra of m-anisaldehyde have been reported in the literature (110,111). The spectra have been interpreted solely by comparison to the spectra of similar molecules. Srivastava (110) proposed assignments for twenty-four of the phenyl modes, eight of the methoxyl modes and four of the formyl

modes. Dwivedi (111) suggested assignments for twenty-six of the m-anisaldehyde modes, nineteen as phenyl modes, three as formyl modes and four as methoxyl modes. Assignments for several of the substituent modes were also proposed in studies of other compounds containing these substituents.

EXPERIMENTAL

SAMPLE PREPARATION

4-Hydroxybenzaldehyde, guaiacol, and m-anisaldehyde were purchased from Aldrich Chemical Company, Inc. All three were purified prior to recording their spectra using the techniques recommended by Perrin (112).

4-Hydroxybenzaldehyde was recrystallized from distilled water containing some H_2SO_3. It was dried over P_2O_5 under vacuum. The resulting crystals were then sublimed, and stored over P_2O_5, under vacuum. The melting point of these white crystals was 114.4-116°C, corresponding to a literature value of 115-116°C (112).

Guaiacol was purified using a simple distillation. The final fraction was collected at 203.5°C at 727mm Hg (205.1°C, 760mm Hg). The boiling point of guaiacol is reported to be 205.05°C at 760mm Hg (113).

m-Anisaldehyde was purified by a vacuum distillation under nitrogen. The distillation was carried out at 12 torr. The final fraction was collected at 121°C. At 11 torr the boiling point is reported to be 117°C (112).

These compounds were characterized by comparison to their infrared spectra published by Sadtler (61) in the 400-4000 cm^{-1} range. They were also compared to other published spectra.

MEASUREMENT OF SPECTRA

Infrared spectra of guaiacol and m-anisaldehyde were recorded for pure liquid samples and for carbon tetrachloride and carbon disulfide solutions of these compounds. The pure sample spectra were recorded for the liquid between NaCl windows. The solutions were measured on a 6% w/v solution in a 0.0225 mm fixed NaCl cell. The infrared spectrum of 4-hydroxybenzaldehyde was recorded on the solid as a KBr pellet. The spectra were recorded using a Nicolet FT-IR over the range 400-4000 cm^{-1}.

Raman spectra of guaiacol and m-anisaldehyde were recorded for the pure liquid samples and for carbon tetrachloride and methanol solutions. The Raman spectra of solid 4-hydroxybenzaldehyde and of methanol and water solutions of 4-hydroxybenzaldehyde were measured. These spectra were measured with the sample in capillary tubes with the scattered radiation viewed 90° from the incident beam. The unpolarized, and both the parallel and perpendicularly polarized spectra were recorded from 50-3800 cm^{-1}. These spectra were obtained using a Jobin Yvon Ramanor HGS2 spectrometer. The 514.5 nm line of an argon ion laser was used as the radiation source. The instrumentation for these measurements was as specified for the monosubstituted benzenes (Table VII).

EXPERIMENTAL RESULTS

The vibrational spectra of the disubstituted benzene derivatives, 4-hydroxybenzaldehyde, guaiacol and m-anisaldehyde are reproduced in Fig. 17-19. The corresponding band positions are tabulated in Tables XXXII-XXXIV. Infrared and Raman solution spectra for the disubstituted benzenes are included in Appendix

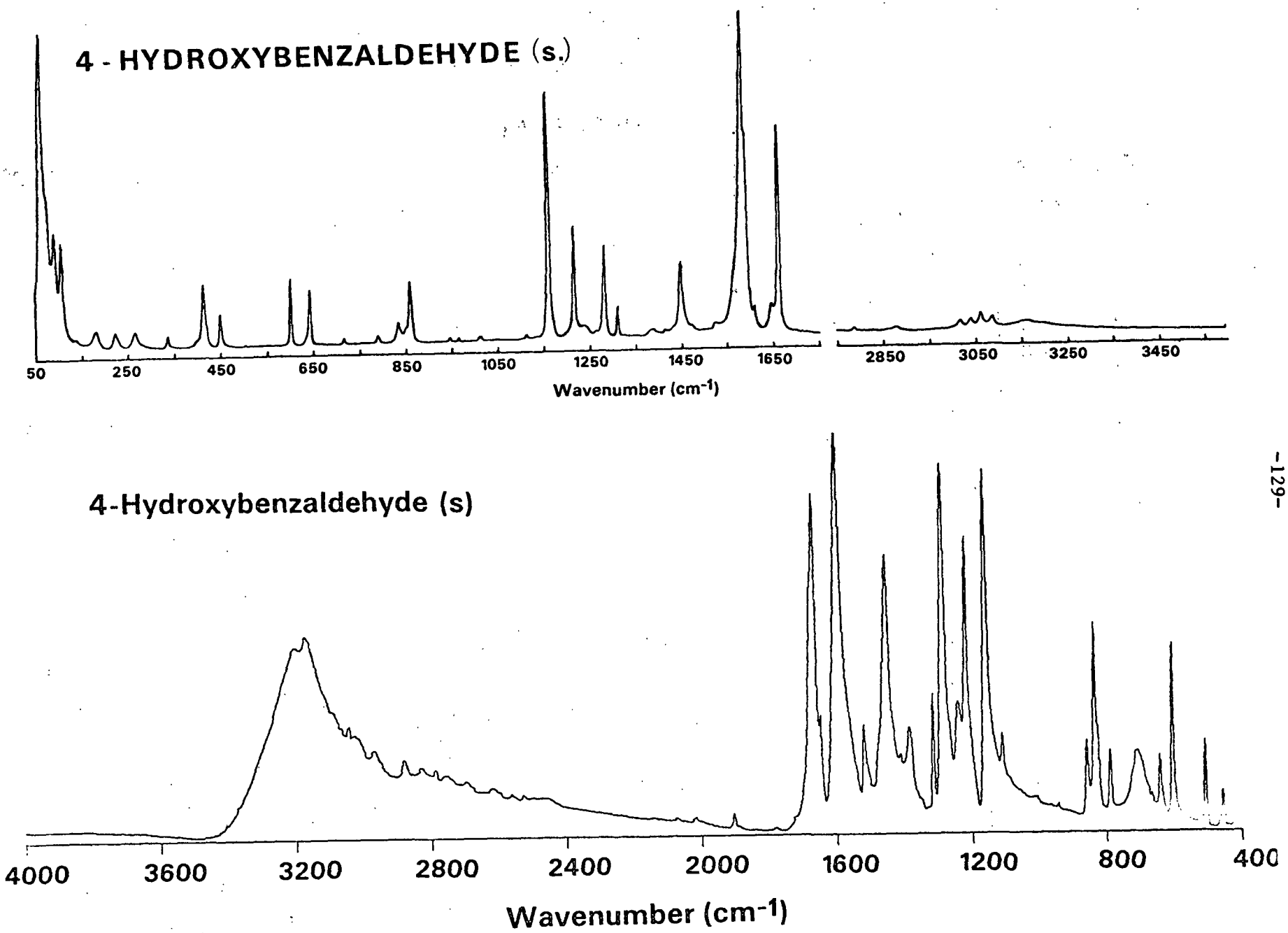


Figure 17. The Raman (upper) and infrared (lower) spectra of 4-hydroxybenzaldehyde.

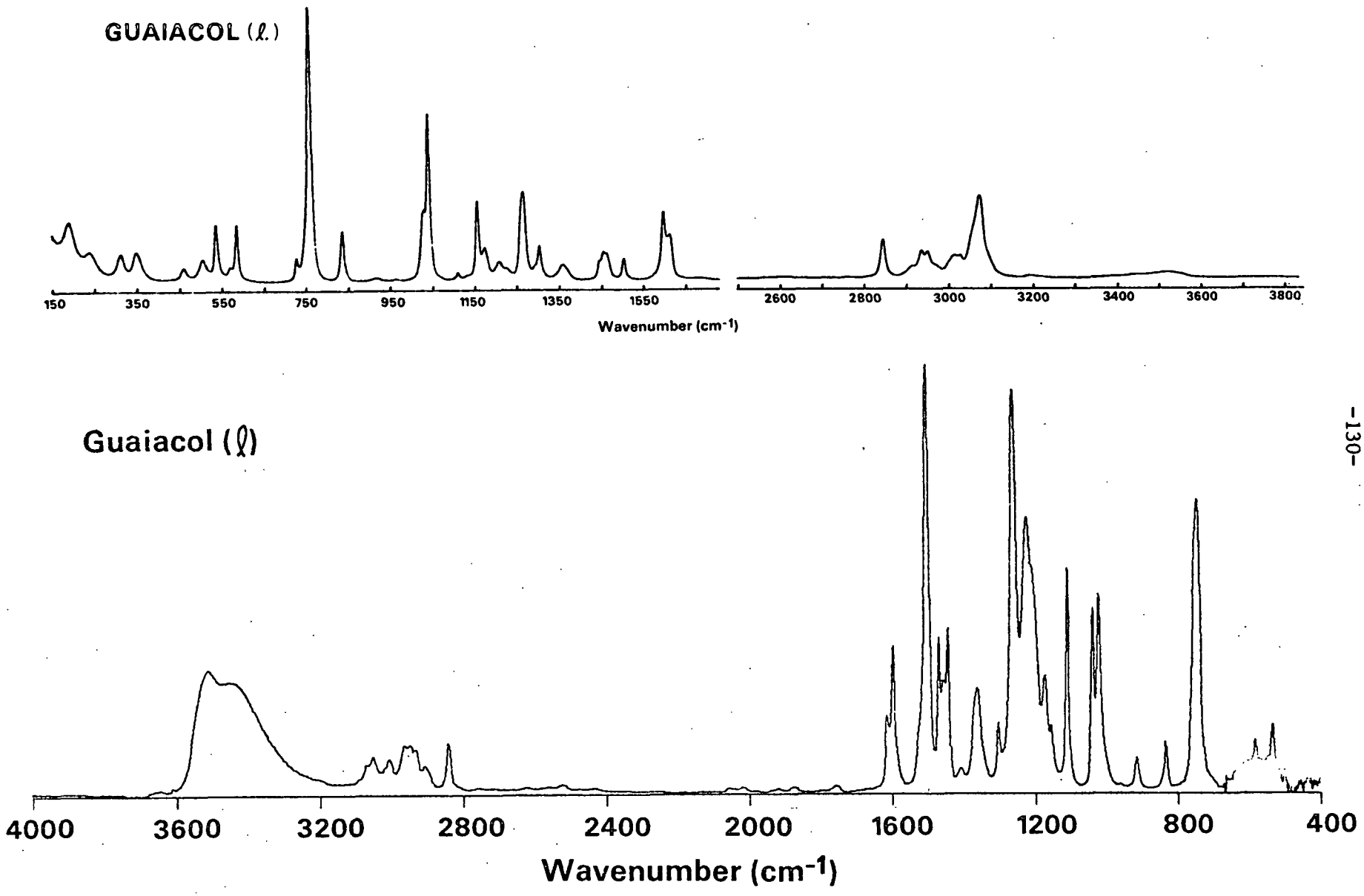
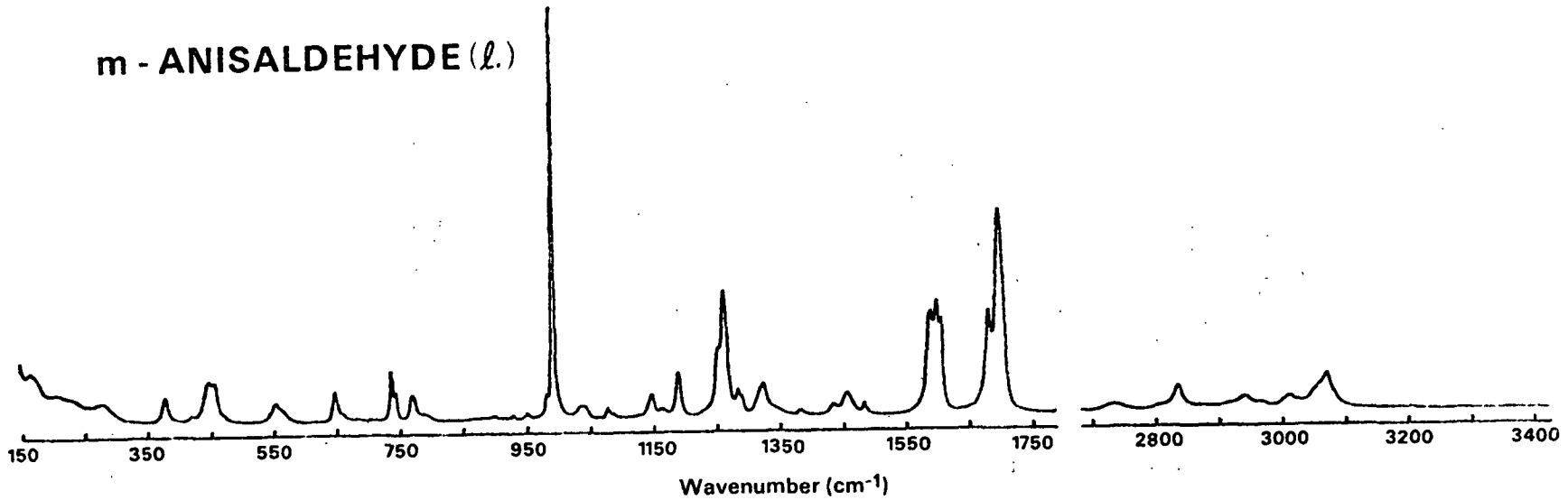


Figure 18. The Raman (upper) and infrared (lower) spectra of guaiacol.



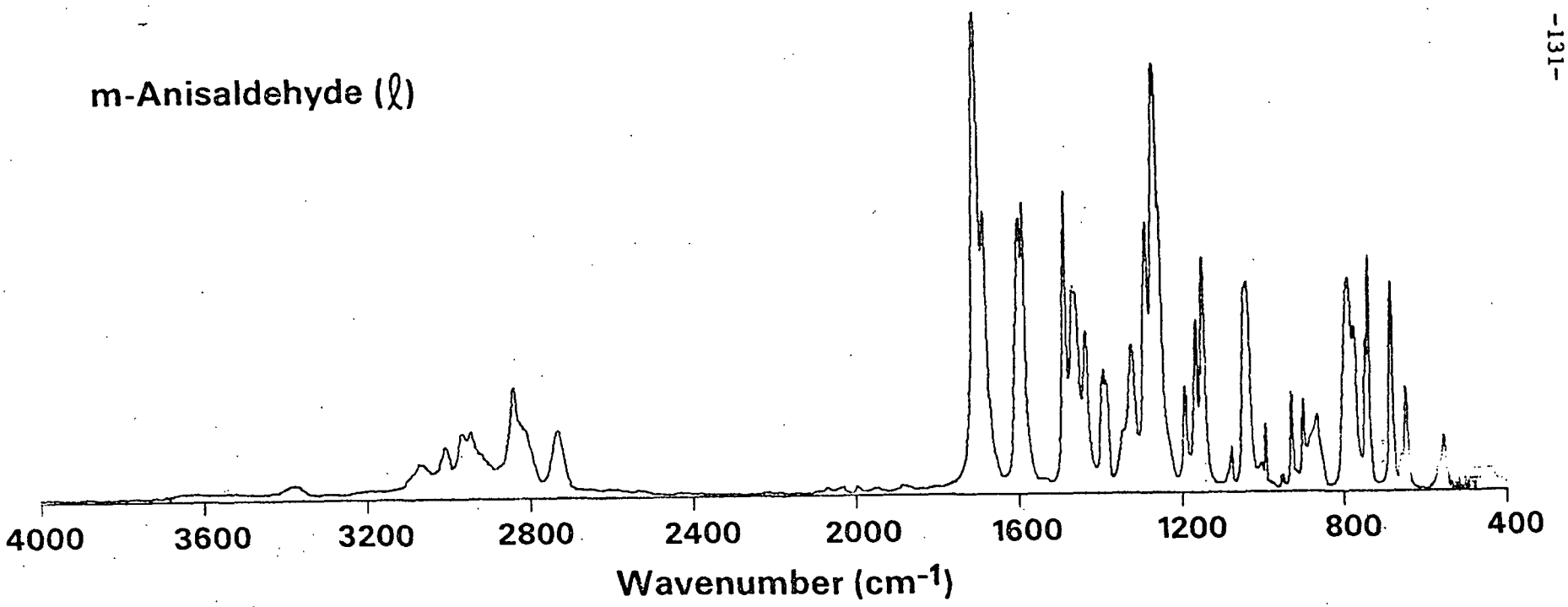


Figure 19. The Raman (upper) and infrared (lower) spectra of m-anisaldehyde.

TABLE XXXII

SPECTRAL DATA - 4-HYDROXYBENZALDEHYDE (SOLID)

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	64 s[a]		1434 sh
	90 m	1452 s	1450 w
	106 m		1475 sh
	138 w	1519 m	1523 w
	179 w	1598 s	1584 w
	222 w		1591 sh
	264 w		1612 w
	337 w	1648 m	1647 w
	349 sh	1666 s	1665 s
	399 sh	2696 w	
	415 m	2754 w	
456 m	451 m	2789 w	2786 w
507 m	506 w	2828 w	
	515 w	2879 w	2876 w
	552 w	2967 m	
604 ms	604 m	3022 m	3018 w
643 m	645 m	3044 m	3042 w
667 w	664 vw		3063 w
708 m	708 w		3086 w
716 sh		3170 m	3171 w
790 m	789 w	3195 m	
825 sh			
835 ms	836 m		
	850 sh		
859 m	861 m		
946 w	947 w		
964 w	965 w		
1009 w	1010 w		
1014 w	1015 w		
	1030 w		
	1050 w		
	1062 w		
1113 m	1112 w		
1140 sh			
1161 s	1162 s		
1218 s	1217 m		
1240 m	1237 w		
	1263 sh		
1286 s	1286 m		
1315 m	1315 m		
	1331 sh		
1387 m	1388 w		
1412 m	1415 w		

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

TABLE XXXIII

SPECTRAL DATA - GUAIACOL (LIQUID)

Infrared, cm-1	Raman, cm-1	Infrared, cm-1	Raman, cm-1
	188 m[a]		1292 sh
	236 m	1303 m	1301 m
	310 m	1361 m	1357 m
	346 m	1410 w	
	456 m	1444 s	1443 m
	502 m	1458 m	1454 m
516 w			1461 m
524 w		1470 s	
533 m	534 m	1502 vs	1502 m
548 w		1597 s	1596 s
572 w	570 m	1615 m	1609 m
584 m	583 m		1681 w
622 w		2843 m	2840 m
	727 m	2909 w	2910 w
746 s		2935 m	2931 w
	759 vs	2950 m	2944 w
834 m	834 m	2964 m	2965 sh
917 m	913 w	3008 m	3009 w
960 w	962 w		3023 w
1024 s	1027 s	3054 m	3053 sh
1040 s	1038 s	3070 w	3070 m
1110 s	1109 w	3443 w	
	1134 sh	3449 m	
1156 m	1155 s	3454 m	
1173 m	1172 m	3467 m	
1208 sh	1206 m	3470 m	
1225 s	1223 w	3510 m	3514 w
1261 vs	1263 s		

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

III. The principal features of the spectra recorded for the dilute solutions of these compounds are very similar to those of the spectra of the pure compounds. The principal differences are due to changes in the extent of hydrogen bonding.

VIBRATIONAL ANALYSIS

The force fields developed for the monosubstituted benzenes were used to calculate the frequencies of the normal modes of the disubstituted benzenes under investigation. Both the kinetic and potential energy matrices were constructed using parameters established for the monosubstituted compounds.

TABLE XXXIV

SPECTRAL DATA - m-ANISALDEHYDE (LIQUID)

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	167 m[a]	1254 s	1253 m
	209 m		1262 s
	230 m	1266 vs	
	279 m	1286 s	1285 m
	379 m		1291 sh
	422 w	1324 m	1324 m
437 vw		1345 sh	
441 w		1385 m	1384 w
447 vw	447 m	1394 m	
	456 m	1436 m	1435 m
464 vw		1460 s	1457 m
470 vw	470 sh	1466 s	
476 vw		1486 s	1484 m
482 w		1533 vw	
490 vw		1544 vw	
503 vw		1587 s	1589 s
554 m	554 m	1597 s	1599 s
	565 m		1606 s
647 m	648 m	1684 s	1682 s
660 w	661 w	1703 s	1699 s
683 s	684 w		2001 w
738 s	738 m	2731 m	
745 m	745 m	2810 sh	2806 w
774 m	770 m	2840 m	2835 m
789 s	788 w		2869 vw
868 m	871 w	2881 w	
ca. 890 sh	887 w		2919 vw
901 m	901 w	2943 m	2941 w
917 w	917 w	2964 m	2963 vw
930 m	930 w	3007 m	
952 w	952 w		3012 w
	983 m	3035 m	
993 mw	994 vs	3064 w	3060 sh
1005 w	1002 w	3071 w	3070 m
1040 s	1037 m		3181 vw
1049 sh	1043 m	3358 vw	
1079 w	1079 m	3364 vw	
	1087 w	3369 vw	
1149 s	1149 s	3375 vw	
1165 m	1164 m	3389 vw	
1192 m	1191 m		

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

KINETIC ENERGY MATRICES

Molecular Structure

The geometries used for 4-hydroxybenzaldehyde, guaiacol and m-anisaldehyde are composites of the structures used for phenol, benzaldehyde and anisole. The standard ring geometry is coupled with the structural parameters of the hydroxyl, formyl and methoxyl groups. These parameters are unchanged from those listed in Table XI. The disubstituted benzenes are assumed to be planar.

Experimentally determined structures for guaiacol and m-anisaldehyde were not found in the literature. Structures adopted for these molecules in other investigations are composites of the geometries of similar molecules, and do not differ significantly from the structures employed in this study. The crystal structure of 4-hydroxybenzaldehyde has been determined (114). This structure shows 4-hydroxybenzaldehyde to be planar within 0.04 Å. The only major difference between the structure assumed in this investigation and that determined by Iwasaki (114) is the COH angle of the hydroxyl group, 118° vs. 109°, respectively. Iwasaki's structure is not used so that the force constants developed for the monosubstituted benzenes can be used in the calculation of the normal vibrations of 4-hydroxybenzaldehyde.

Internal Coordinates

The internal coordinates for the disubstituted benzenes are defined as they were for the monosubstituted compounds. The internal coordinates for the substituent groups are combined with the internal coordinates used for the phenyl group.

A set of fifty-three internal coordinates are used to describe 4-hydroxybenzaldehyde. The thirty-seven coordinates used to define the in-plane problem

comprises twenty-four phenyl coordinates, eight formyl coordinates and five hydroxyl coordinates. The internal coordinates for the phenyl group include the six CC bonds, the six CCC angles, the four (unsubstituted) CH bonds, and the eight CCH angles associated with these CH bonds. The CX bond stretch and the corresponding CCX angles are included with the substituent coordinates. The formyl and hydroxyl coordinates are defined as for benzaldehyde and phenol. Sixteen coordinates define the out-of-plane problem: fourteen phenyl coordinates, four formyl and two hydroxyl coordinates. The phenyl coordinates consist of the six torsions (defined in phi coordinates) and the four (unsubstituted) CH out-of-plane wags. The formyl and hydroxyl coordinates are as defined for benzaldehyde and phenol. The set of thirty-seven in-plane coordinates includes ten redundant coordinates. Three of these are inherent in the cyclical structure. The remaining seven arise from the use of all three angles about each of the seven carbon atoms in this molecule. There are four redundant coordinates in the set of out-of-plane internal coordinates. Again, three are a result of the cyclical structure. The other redundancy lies in the coordinates for the formyl group.

A set of fifty-eight internal coordinates is used to describe guaiacol. This set of coordinates comprises twenty-four in-plane and ten out-of-plane phenyl coordinates, five in-plane and two out-of-plane hydroxyl coordinates, and seventeen methoxyl coordinates. The phenyl coordinates are as described for 4-hydroxybenzaldehyde. The hydroxyl and methoxyl coordinates are the same as those defined for phenol and anisole. This set of fifty-eight internal coordinates includes thirteen redundant coordinates. Six of these arise from the necessity of ring closure. The other redundant coordinates are a result of including all of the angles about each carbon atom in the molecule.

Sixty-three internal coordinates define the vibrations of m-anisaldehyde. Twenty-four in-plane and ten out-of-plane phenyl coordinates, eight in-plane and four out-of-plane formyl coordinates and seventeen methoxyl coordinates are used. The formyl and methoxyl coordinates are as described for benzaldehyde and anisole. The phenyl coordinates are as detailed for 4-hydroxybenzaldehyde. Fifteen redundant coordinates are included in this set of sixty-three internal coordinates. These comprise six due to the ring structure and nine due to the overdefinition of the angles about each carbon atom. The internal coordinate definitions for these disubstituted benzenes are listed in Appendix IV.

POTENTIAL ENERGY MATRICES

Modified valence force fields are used to define the potential energy matrices for the disubstituted benzenes. These force fields are set up analogously to the potential energy matrices developed for the monosubstituted benzenes. The values of the force constants are transferred from the force fields developed for phenol, benzaldehyde and anisole.

The modified valence force field established for 4-hydroxybenzaldehyde is a composite of the force fields developed for phenol and benzaldehyde. The in-plane force field comprises twelve valence force constants for the phenyl group, fifteen force constants for the C-CHO group and twelve force constants for the C-OH group. The out-of-plane force field is composed of eight phenyl, five C-OH and seven C-CHO force constants. The interaction force constants for the substituents are those found to be necessary for the monosubstituted compound calculations. The force constants included are those used for phenol and benzaldehyde. No interaction force constants for interactions between the two substituents are included. The values of the phenyl force constants are taken

from the joint refinement of the phenyl force constants (the refinement over all three monosubstituted benzenes). The values of the substituent force constants are from the results of the refinements of the individual compounds.

Sixty-four force constants are used to define a modified valence force field for guaiacol. The force field employs twelve force constants for the in-plane and eight force constants for the out-of-plane modes of the phenyl group, twelve force constants for the in-plane and five force constants for the out-of-plane vibrations of the C-OH group, and twenty-seven force constants for the motions of the C-OCH_3 group. Only the force constants found necessary to calculate the fundamental frequencies of the monosubstituted compounds are used in this force field. No additional interaction force constants, e.g., between substituents, are included. The values of the phenyl force constants are from the joint phenol/benzaldehyde/anisole phenyl refinement. The substituent force constant values are taken from the individual refinements.

A sixty-nine parameter modified valence force field is used to calculate the normal modes of m-anisaldehyde. This force field comprises twelve in-plane phenyl, eight out-of-plane phenyl, fifteen in-plane C-CHO, seven out-of-plane C-CHO, and twenty-seven C-OCH_3 force constants. The force constants used are those determined to be necessary in the monosubstituted benzene calculations. No additional interaction force constants are defined. Values of the force constants are from either the appropriate substituent force field or the phenyl force field determined by the joint refinement.

CALCULATIONS

Once constructed, the kinetic and potential energy matrices are used to calculate the frequencies of the fundamental modes of 4-hydroxybenzaldehyde,

guaiacol and m-anisaldehyde. The force fields for these compounds are not refined. Refinements of the force field for 4-hydroxybenzaldehyde were carried out as a check on this decision. These refinements did not show significant improvement in the average error or potential energy distribution. The results of the normal coordinate calculations are used to assign the IR and Raman spectra of the three disubstituted model compounds. Based on these assignments the twenty-seven in-plane frequencies of 4-hydroxybenzaldehyde are calculated with an average error of 14.15 cm^{-1} or 1.589%. The thirty in-plane fundamentals of guaiacol are reproduced with an average error of 9.26 cm^{-1} or 0.834%. The thirty-two in-plane modes of m-anisaldehyde are calculated with an average error of 13.07 cm^{-1} or 1.849%. The twelve A" modes of 4-hydroxybenzaldehyde, the fifteen A" modes of guaiacol, and the sixteen A" modes of m-anisaldehyde are duplicated with average errors of 6.53 cm^{-1} or 1.625%, 7.96 cm^{-1} or 1.451% and 8.55 cm^{-1} or 1.606%, respectively. As they are unobserved in the vibrational spectra, the frequencies of the in-plane OH stretch of 4-hydroxybenzaldehyde, the $O-CH_3$ torsion of guaiacol, and the C-CHO and $O-CH_3$ torsions of m-anisaldehyde are not included in these errors. The observed and calculated frequencies and the potential energy distributions for these compounds are shown in Tables XXXV-XXXVII. The accuracy of the fit of the calculated to the observed frequencies can be seen in line representations of the spectra (Fig. 20-22). Comparison of the differences between the observed and calculated frequencies of the disubstituted and monosubstituted benzenes shows these differences to be random. There is no particular pattern to these errors, e.g., no one frequency is consistently too high or too low. If Iwasaki's structural parameters are used to calculate the G matrix for 4-hydroxybenzaldehyde, the in-plane frequencies are calculated with an average error of 18.14 cm^{-1} or 1.877%, and the calculated out-of-plane frequencies have an average error of 12.06 cm^{-1} or 2.748%.

TABLE XXXVa

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE IN-PLANE VIBRATIONS OF 4-HYDROXYBENZALDEHYDE

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
3609	3609	0	-0.01	OH P(100)
3086	3074	12	0.37	CH(98)
3063	3073	-10	-0.31	CH(98)
3042	3040	2	0.07	CH(100)
3022	3038	-16	-0.51	CH(100)
2754	2739	15	0.55	CH B(98)
1679	1699	-20	-1.17	CO B(69) CCHB(20)
1598	1614	-16	-0.98	CC(74) CCH(23) CCC(10)
1588	1594	-6	-0.38	CC(78) CCH(12)
1519	1508	12	0.76	CCH(54) CC(36)
1450	1446	4	0.25	CC(36) CCH(28) CCHB(12)
1387	1392	-5	-0.36	CCHB(43) CO B(20) CCH(18)
1315	1344	-29	-2.19	CCH(56) CC(50) COHP(15)
1286	1315	-29	-2.24	CC(67) CCH(44)
1240	1260	-20	-1.60	CO P(38) CCC(27) CCH(17) CC(12)
1218	1196	22	1.77	COHP(31) CC(27) CC B(21) CCH(13)
1162	1174	-12	-1.01	COHP(37) CC(34) CO P(16) CCH(14) CC B(13)
1140	1161	-21	-1.86	CCH(61) CC(24)
1112	1116	-4	-0.37	CCH(48) CC(37)
1015	1011	4	0.41	CC(46) CCH(27) CCC(20)
861	878	-17	-1.94	CC(56) CCC(10)
789	776	13	1.61	CCC(19) CCOB(15) CO P(14) CC B(12) CC(10)
645	620	25	3.83	CCC(62) CCH(16) CC(11)
604	582	22	3.65	CCOB(16) CCC(16) CCCB(14) CO P(13) CCOP(11)
451	441	10	2.30	CCOP(46) CCC(19) CCCB(12)
402	376	26	6.58	CCOP(29) CCC(16) CC B(12) CC(12)
222	209	13	5.79	CCCB(51) CCOB(34)
Average Error		14	1.59	

[a]The internal coordinates are the phenyl CC stretches (CC), CH stretches (CH), CCH bends (CCH) and CCC bends (CCC), the hydroxyl CO stretch (CO P), OH stretch (OH P), CCO bend (CCOP) and COH bend (COHP), and the formyl CC stretch (CC B), CH stretch (CH B), CO stretch (CO B), CCC bend (CCCB), CCH bend (CCHB), and CCO bend (CCOB).

TABLE XXXVb

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE OUT-OF-PLANE VIBRATIONS OF 4-HYDROXYBENZALDEHYDE

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
1010	1009	1	0.09	WAGH(62) WAG(21) WAGO(10)
964	960	4	0.46	WAG(96) TOR(28)
947	949	-2	-0.19	WAG(80) TOR(19) WAGH(16)
835	833	2	0.26	WAG(88) TOR(12)
825	828	-3	-0.36	WAG(87) TOR(20)
667	679	-12	-1.75	TOR(34) WAGP(31) WAGC(14)
507	514	-7	-1.43	WAGP(55) WAGC(24) TOR(10)
415	423	-8	-1.96	TOR(41) WAG(15) TORP(10)
349	353	-4	-1.17	WAGC(34) TOR(28) TORP(11)
337	307	30	8.80	TORP(78) TOR(12)
179	184	-5	-3.02	TORB(46) TOR(32)
106	106	0	0.02	TORB(44) TOR(28)
Average Error		7	1.62	

[a]The internal coordinates are the phenyl wags (WAG) and torsions (TOR); the hydroxyl wag (WAGP) and torsion (TORP); and the formyl wag (WAGC), CH wag (WAGH), CO wag (WAGO), and torsion (TORB).

INTERPRETATION OF SPECTRA

The potential energy distributions calculated using the force fields aid in the interpretation of the vibrational spectra of the disubstituted benzenes. The assignments of these bands are compared to ascertain the effect of disubstitution on the fundamental modes of benzene and the substituent modes. This comparison and the assignment of the fundamental modes of the disubstituted compounds are presented in this section.

Spectral Assignments

The IR and Raman spectra of 4-hydroxybenzaldehyde, guaiacol and m-anisaldehyde are assigned in this investigation using Raman band intensities, depolarization ratios and the results of the normal coordinate calculations as reflected in the potential energy distributions. Only the OH stretching and the CH stretching modes are "pure" modes involving just one internal coordinate or just one

TABLE XXXVIa

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE IN-PLANE VIBRATIONS OF GUAIACOL

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
3556	3609	-53	-1.50	OH P(100)
3091	3085	6	0.20	CH(97)
3070	3066	4	0.13	CH(98)
3054	3044	10	0.31	CH(100)
3023	3029	-6	-0.19	CH(101)
2950	2951	-1	-0.04	CH M(99)
2840	2835	5	0.19	CH M(100)
1615	1623	-8	-0.51	CC(72) CCH(16) CCC(11)
1596	1593	4	0.22	CC(80) CCH(15) CCC(9)
1502	1487	15	0.98	CCH(55) CC(38)
1470	1471	-1	-0.05	CCH(39) CC(27) OCHM(16) HCHM(11)
1461	1464	-3	-0.20	OCHM(50) HCHM(31) CCH(12)
1454	1443	11	0.79	HCHM(76) OCHM(17)
1357	1352	5	0.39	CCH(45) CC(41) COHP(24)
1301	1308	-7	-0.56	CC(69) CCH(36) CO P(9)
1263	1272	-9	-0.70	CO M(26) CC(24) CCC(16) CCH(11) COHP(9)
1223	1221	2	0.19	CO P(24) CC(24) CCH(23) CO M(13)
1208	1173	35	2.91	CCH(49) COHP(21) CC(14)
1172	1166	6	0.51	CC(42) CCH(36) COHP(23)
1134	1118	16	1.44	OCHM(32) CCH(28) CC(21)
1109	1100	9	0.83	OCHM(39) CC(17) CCH(17)
1040	1040	0	-0.03	OC M(58) CC(17) CCH(11)
1027	1027	0	-0.01	CC(55) CCH(17) OC M(10)
834	843	-9	-1.08	CCC(42) CO P(19) CCH(11) CC(11)
786	781	5	0.60	CC(28) CO M(24) CCC(19) COCM(11)
583	564	19	3.23	CCC(45) COCM(14) CC(13) CCOM(12) CCH(10)
534	528	6	1.14	CCOP(29) COCM(27) CCOM(21) CC(13)
502	491	11	2.24	CCC(37) CO P(16) CCOP(13) COCM(11)
346	343	3	0.81	CCOP(35) COCM(30)
236	229	7	3.04	CCOM(50) CCOP(14) COCM(13)
Average Error		9	0.83	

[a]The internal coordinates are the phenyl CC stretches (CC), CH stretches, CCH bends (CCH) and CCC bends (CCC); the hydroxyl CO stretch (CO P), OH stretch (OH P), CCO bend (CCOP) and COH bend (COHP); and the methoxyl CO stretch (CO M), OC stretch (OC M), CH stretches (CH M), CCO bend (CCOM), HCH bends (HCHM), OCH bends (OCHM) and COC bend (COCM).

type of internal coordinate. The remaining modes have substantial mixing of the internal coordinates. A band is generally assigned to the coordinate making the major contribution. The assignment of the bands whose literature assignment has varied or whose assignment in this investigation differs from that reported in the literature, and the assignments of the substituent modes, will be discussed in this section.

TABLE XXXVIb

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE OUT-OF-PLANE VIBRATIONS OF GUAIACOL

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate (%)
2965	2951	14	0.48	CH M(99)
1443	1441	2	0.13	HCHM(78) OCHM(22)
1155	1155	0	0.00	OCHM(77) HCHM(21)
962	981	-19	-1.99	WAG(100) TOR(28)
917	936	-19	-2.08	WAG(94) TOR(26)
852	861	-9	-1.10	WAG(88) TOR(19)
759	767	-8	-1.00	WAG(83) TOR(11)
741	738	3	0.42	WAGM(35) WAGP(29) WAG(20) TOR(15)
570	568	2	0.41	TOR(33) WAG(13) WAGP(10) WAGM(9)
456	452	4	0.88	WAGP(35) WAGM(31) TOR(20)
346	356	-10	-2.98	TORP(56) TOR(12)
310	286	24	7.87	TORP(40) TORM(27) TOR(26)
236	235	2	0.64	TORM(54) TOR(18) WAGM(12)
188	187	1	0.53	TOR(47) TORO(11) TORM(10)
(108)	107	1	1.25	TORO(96) TOR(13)
Average Error		8	1.45	

[a]The internal coordinates are the phenyl wags (WAG) and torsions (TOR), the methoxyl wag (WAGM), CH stretch (CH M), HCH bend (HCHM), OCH bend (OCHM), C-OCH_3 torsion (TORO) and CO-CH_3 torsion (TORM), and the hydroxyl wag (WAGP) and torsion (TORP).

4-Hydroxybenzaldehyde

In a study of para-substituted phenols, Jakobsen and Brewer (102) assigned the phenyl and hydroxyl vibrations in the 150-1700 cm^{-1} region of the vibrational spectra of 4-hydroxybenzaldehyde. Assignments were made by comparison to the

TABLE XXXVIIa

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE IN-PLANE VIBRATIONS OF m-ANISALDEHYDE

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
3071	3081	-10	-0.33	CH(97)
3060	3057	3	0.11	CH(99)
3056	3055	1	-0.03	CH(99)
3035	3032	3	0.10	CH(100)
2941	2951	-10	-0.35	CH M(99)
2835	2835	0	0.01	CH M(100)
2731	2739	-8	-0.28	CH B(98)
1699	1699	0	0.01	CO B(68) OCHB(20)
1599	1631	-32	-2.03	CC(75) CCH(16) CCC(9)
1589	1606	-17	-1.08	CC(73) CCH(18)
1486	1500	-14	-0.94	CCH(46) CC(38)
1466	1479	-13	-0.90	CCH(38) CC(37)
1460	1465	-5	-0.31	OCHM(63) HCHM(39)
1435	1442	-7	-0.52	HCHM(76) OCHM(18)
1385	1394	-9	-0.62	OCHB(49) CO B(21)
1324	1331	-7	-0.55	CCH(77) CC(54)
1286	1312	-26	-2.01	CC(78) CCH(25)
1266	1278	-12	-0.92	CO M(31) CCH(18) CCC(18) CC(18) CC B(12)
1192	1171	21	1.77	CCH(58) CC(12) CC B(10)
1149	1163	-14	-1.25	CCH(38) CC(20) CC B(11)
1087	1118	-31	-2.85	OCHM(58) HCHM(11) CCH(11) CC(9)
1079	1092	-13	-1.18	CCH(38) CC(33)
1040	1047	-7	-0.68	OC M(49) CC(19) CCH(13) CCC(11)
994	1010	-16	-1.62	CC(49) CCC(24)
983	968	15	1.55	CC(27) CC B(15) CO M(15)
745	744	1	0.08	CCC(29) CC(18) CO M(11)
647	671	-24	-3.77	CCC(29) COCM(13) CC(12) CCOB(11) CCCB(9)
554	582	-28	-5.05	CCC(26) CC(21) COCM(14) CCOB(9)
470	380	-10	-2.08	CCC(22) CO M(17) CCOM(10) CC(10)
458	442	16	3.40	CCCB(27) CCC(20) CC B(16) CC(10)
230	252	-22	-9.58	COCM(31) CCOB(28) CCCB(26)
167	145	22	13.18	CCOM(45) COCM(33) CCCB(25) CCOB(11)
Average Error		13	1.85	

[a]The internal coordinates are the phenyl CC stretches (CC), CH stretches (CH), CCH bends (CCH) and CCC bends (CCC); the methoxyl CO stretch (CO M), OC stretch (OC M), CH stretch (CH M), CCO bends (CCOM), HCH bends (HCHM), OCH bends (OCHM) and COC bend (COCM); and the formyl CC sketch (CC B), CH stretch (CH B), CO stretch (CO B), CCC bend (CCC B), CCH bend (CCHB), and CCO bend (CCOB).

spectra of other substituted benzenes supplemented by dilution effects. Jakobsen found that sixteen of the twenty-five phenyl fundamentals studied were relatively constant on disubstitution. Of the nine substituent sensitive modes, four were unaffected by a change in the p-substituent of p-substituted phenols. Apparently they are governed by the motion of only one of the two substituents. Martin, Moller, and Nishimura (103) assign thirty of the fundamental modes of 4-hydroxybenzaldehyde. The majority of their assignments agree with those of Jakobsen, with the exception of mode 12.

TABLE XXXVIIb

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE IN-PLANE VIBRATIONS OF m-ANISALDEHYDE

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
2964	2951	13	0.45	CH M(99)
1436	1441	-5	-0.36	HCHM(78) OCHM(22)
1164	1155	9	0.77	OCHM(77) HCHM(21)
1005	1004	1	0.06	WAGO(65) WAG(18) WAGH(10)
952	972	-20	-2.08	WAG(92) TOR(26)
901	905	-4	-0.39	WAG(81) TOR(20) WAGO(9)
868	883	-15	-1.75	WAG(94) TOR(23)
788	784	4	0.55	WAG(92) TOR(13)
684	674	10	1.41	TOR(30) WAGM(28) WAG(13) WAGC(13)
518	526	-8	-1.60	WAGM(60) WAGC(18) TOR(15)
447	446	1	0.17	WAGC(33) TOR(31) WAG(9)
279	285	-6	-2.28	TORM(42) TOR(34)
230	246	-16	-7.10	TOR(28) TORM(22) TORB(16)
209	202	7	3.51	TORM(33) TOR(23)
134	135	-1	-0.40	TORM(55) TORO(30) WAGC(9)
97	97	0	-0.43	TORO(74) TOR(16) TORB(16)
Average Error		8	1.46	

[a]The internal coordinates are the phenyl wags (WAG) and torsions (TOR); the formyl wag (WAGB), CH wag (WAGH), CO wag (WAGO) and torsion (TORB); and the methoxyl wag (WAGM), CH stretch (CH M), HCH bend (HCHM), OCH bend (OCHM), C-OCH_3 torsion (TORO) and CO-CH_3 torsion (TORM).

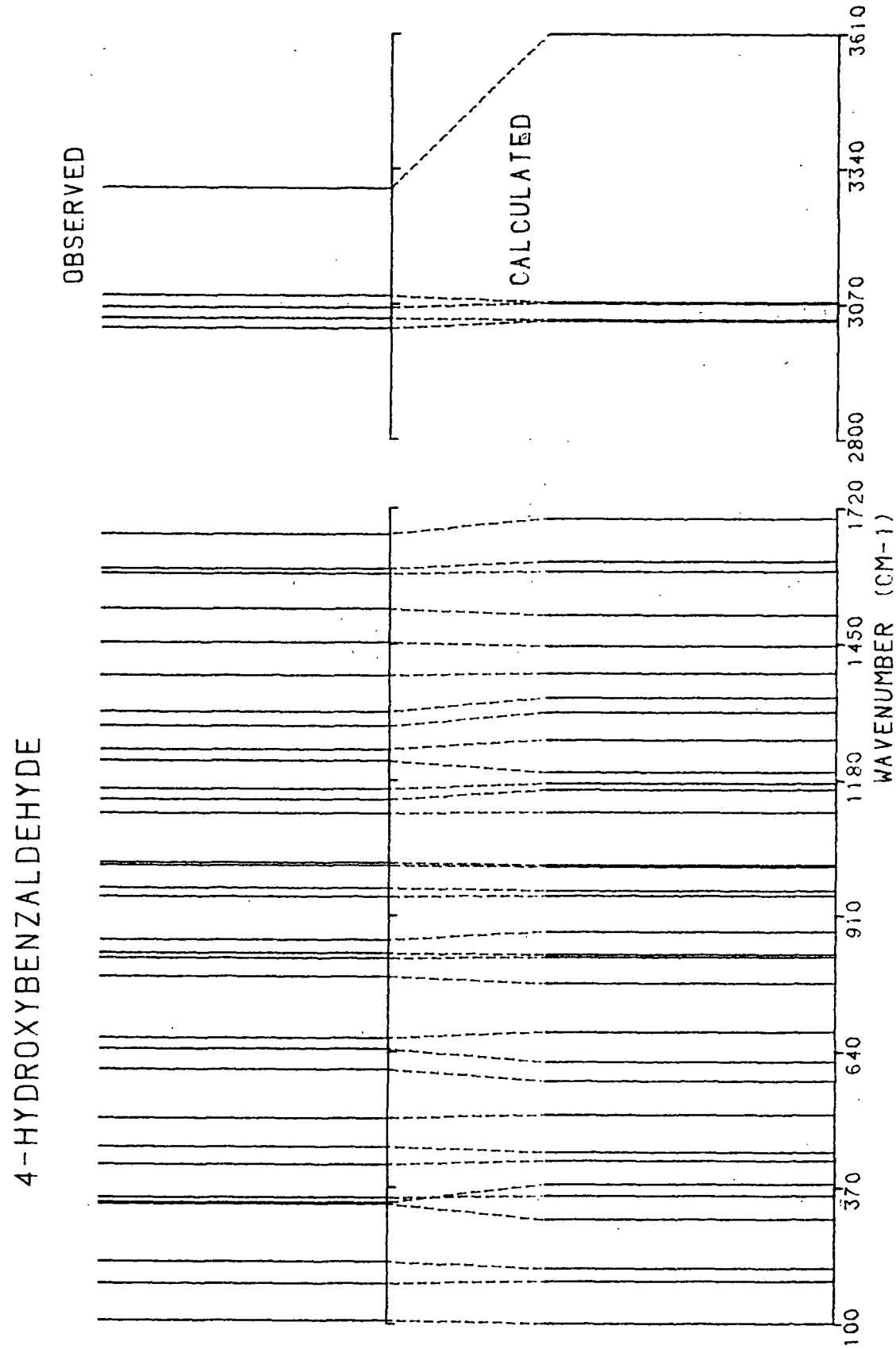


Figure 20. Comparison of the observed and calculated modes of 4-hydroxybenzaldehyde.

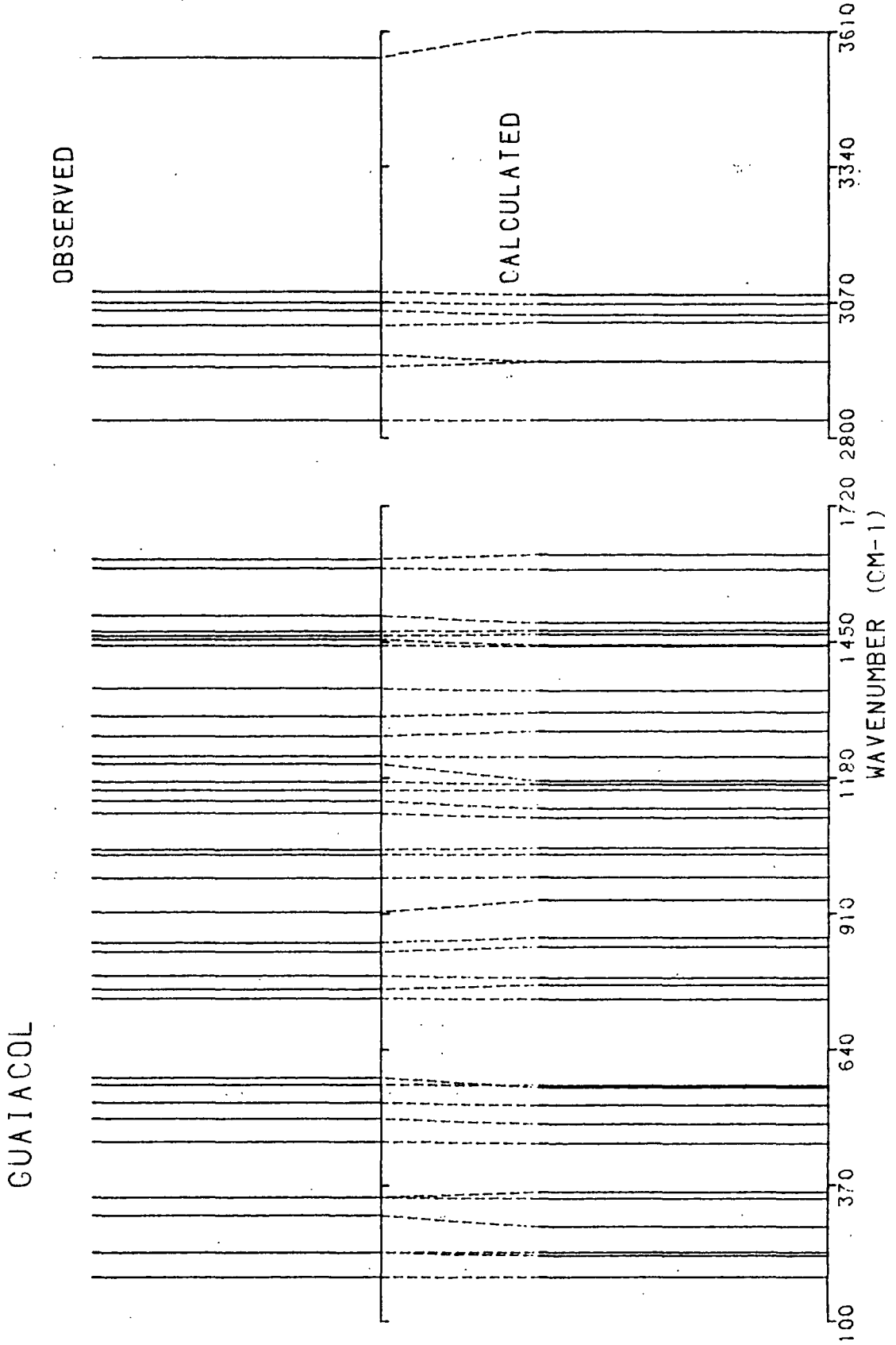


Figure 21. Comparison of the observed and calculated modes of guaiacol.

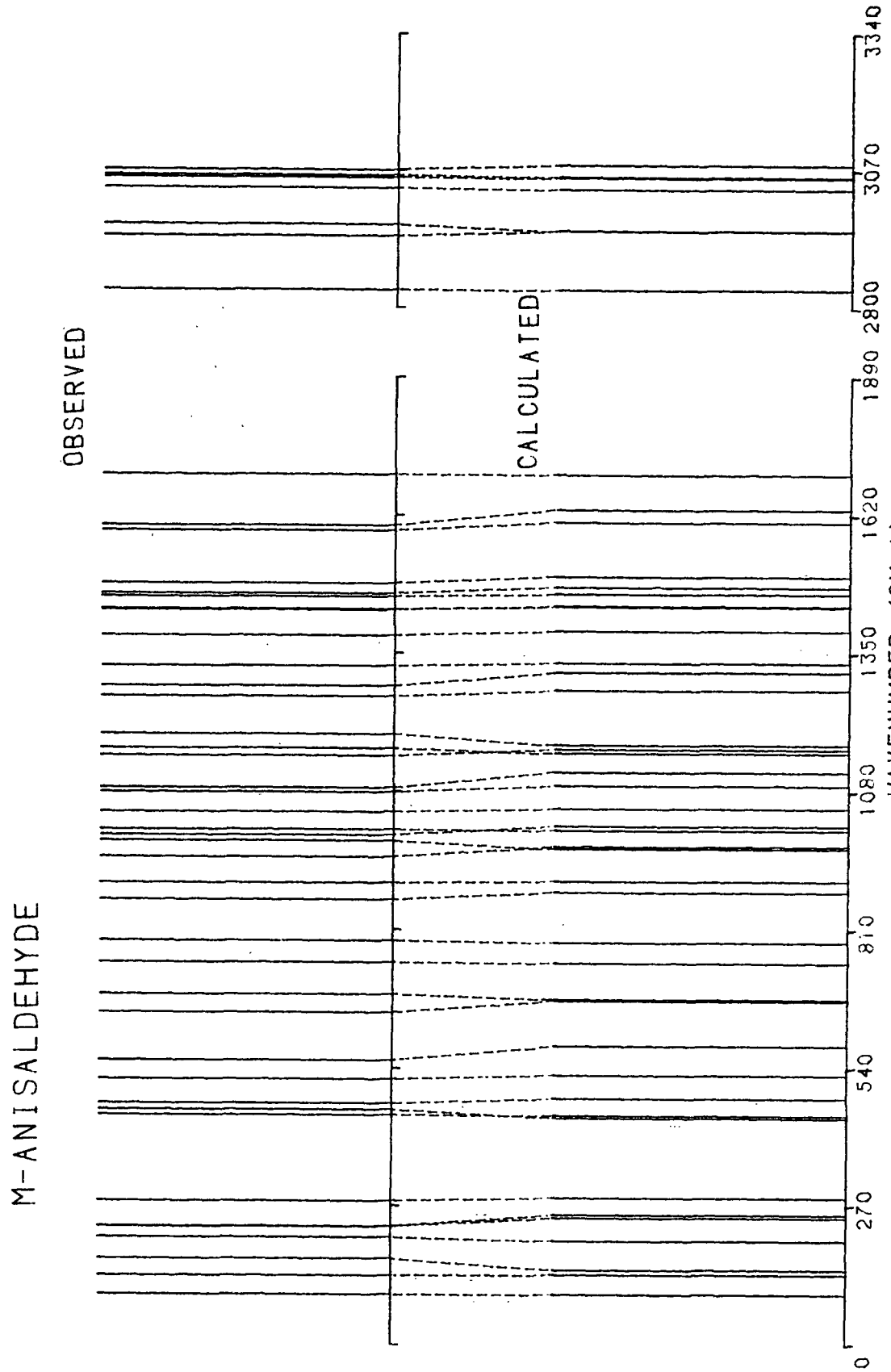


Figure 22. Comparison of the observed and calculated modes of m-anisaldehyde.

The assignments of the phenyl modes made in this investigation agree with the majority of Jakobsen's (102) and Martin's (103) assignments. The exceptions are the in-plane and out-of-plane C-OH bends and the out-of-plane C-CHO bend. Of the substituent modes the in-plane COH bend, the C=O stretch and the C-CHO torsion have differing assignments.

The vibration derived from benzene mode 12 was assigned at 718 cm^{-1} by Martin and at 791 cm^{-1} by Jakobsen. The normal coordinate calculations place this mode at 776 cm^{-1}. It is assigned to a band of medium intensity at 789 cm^{-1} in agreement with Jakobsen (102).

The in-plane and out-of-plane C-OH bends and the out-of-plane C-CHO bend were assigned by Martin (103) at 181, 342, and 204 cm^{-1}, respectively. In the monosubstituted compounds discussed in Chapter II these modes were assigned to bands at 413, 509, and 451 cm^{-1}. Based on the potential energy distribution for 4-hydroxybenzaldehyde these vibrations are calculated to arise at 441, 514, and 353 cm^{-1}. The in-plane and out-of-plane C-OH bends and the out-of-plane C-CHO bend are therefore assigned to the bands occurring at 451, 507, and 349 cm^{-1}.

In addition to thirty phenyl fundamental modes, 4-hydroxybenzaldehyde has three hydroxyl fundamental vibrations. As in phenol, the three hydroxyl modes are the OH stretching mode, the COH in-plane bend, and the COH out-of-plane bend, or torsion. In phenol these were assigned at 3615, 1180 (and 1344) and 310 cm^{-1} in free hydroxyl groups and at 3300, 1180 (and 1344), and 700 cm^{-1} in hydrogen-bonded hydroxyl groups. In the spectra of 4-hydroxybenzaldehyde these modes were previously assigned to absorptions at 3594 (104), 1219 (102), and 349 cm^{-1} (105) for free hydroxyl groups. The rise in the frequency of the torsion of the hydroxyl group relative to its position in phenol (349 cm^{-1} vs. 310 cm^{-1})

was explained by changes in the double bond character of the CO bond. When an electron-withdrawing group, such as -CHO is substituted on the aromatic ring para to the hydroxyl group, the π-electron donation by the hydroxyl group increases. This increases the double bond character of the CO bond, thereby increasing the torsional barrier and frequency (105). Analogously, it was suggested that the hydroxyl stretching frequency is lowered as the electron-attracting nature of the substituent increases due to the increased positive charge on the oxygen atom (104). Aihara (106) assigned the intermolecularly bonded COH in-plane and out-of-plane bending modes to bands at 1240 and 712 cm^{-1}. These assignments were based on the behavior of the bands with a rise in temperature. Martin, et al. (103) assigned the COH in-plane bend at 1166 cm^{-1}.

In this investigation a free hydroxyl OH stretching band is not observed. A broad band centered at 3300 cm^{-1} is attributed to a hydrogen-bonded OH stretch. The calculations support the assignment of the free OH stretch at ca. 3600 cm^{-1}. The potential energy distribution shows considerable contribution of the in-plane COH bend to two bands, at 1218 cm^{-1} and 1160 cm^{-1}. The 1218 cm^{-1} band also has a substantial contribution from the C-CHO stretch. For this reason the in-plane COH bend is assigned to the 1162 cm^{-1} band in agreement with Martin (103). Jakobsen (102) attributed a band at 708 cm^{-1} to the COH torsion. This frequency is appropriate for a hydrogen-bonded torsion. The normal coordinate calculations indicate that the free COH torsion should occur at 307 cm^{-1}. A weak band at 337 cm^{-1} in a Raman solution spectrum is assigned to this mode.

The remaining fundamental modes of 4-hydroxybenzaldehyde are the six formyl modes: the CH stretch, the C=O stretch, the in-plane CCH and CCO bending

modes, the out-of-plane CH wag and the torsion about the C-CHO bond. All but the in-plane CCO bending mode were previously assigned in 4-hydroxybenzaldehyde.

As in benzaldehyde, two absorption bands are observed between 2600 cm^{-1} and 2900 cm^{-1} where the aldehydic CH stretching vibration should occur. Again these were interpreted as resulting from a Fermi resonance interaction between the aldehydic CH stretching fundamental and the first overtone of the aldehydic CH bending vibration (44,46). The band at 2730 cm^{-1} was assigned as the CH stretch. Berthelot (107) attributed the band at 1716 cm^{-1} to the C=O stretching mode. However, Aihara (106) assigned this mode to a band at 1666 cm^{-1}. Campagnaro (57) in his study of torsional barriers in aromatic systems assigned the CHO torsion to a band at 128 cm^{-1}. In benzaldehyde the CH stretch, the C=O stretch and the CHO torsion of the formyl group were assigned to absorptions occurring at 2730, 1707, and 127 cm^{-1}, respectively. Martin (103) assigned the in-plane CCH bending mode and the out-of-plane aldehyde hydrogen wag to bands at 1463 and 1016 cm^{-1}. These modes were assigned at 1394 and 1008 cm^{-1} in benzaldehyde. The in-plane CCO bending mode has not been assigned for 4-hydroxybenzaldehyde, but was assigned at 649 cm^{-1} in benzaldehyde.

In the normal coordinate calculations for 4-hydroxybenzaldehyde in this investigation the CH stretching band of the formyl group is calculated to arise at 2739 cm^{-1}, the C=O stretch is calculated to occur at 1699 cm^{-1}, the C-CHO torsion at 106 cm^{-1}, the CCH in-plane and out-of-plane bends at 1392 and 1009 cm^{-1} and the in-plane HCO bend at 582 cm^{-1}. These modes are assigned to bands at 2754, 1666, 106, 1387, 1010, and 604 cm^{-1}, respectively. The proposed assignment of the vibrational spectra of 4-hydroxybenzaldehyde is presented in Table XXXVIII.

TABLE XXXVIII

ASSIGNMENTS OF THE NORMAL MODES OF 4-HYDROXYBENZALDEHYDE

Infrared, cm^{-1}	Raman, cm^{-1}	Assignments
	106 m[a]	A" CHO torsion
	179 w	16b A" ring deformation
	222 w	9b A' CCX bend
	337 w	A" OH torsion
		6a A' ring deformation
	349 sh	11 A" CCX bend
	402 m	6a A' ring deformation
	415 m	16a A" ring deformation
456 m	451 m	15 A' CCX bend
507 m	506 w	10b A" CCX bend
604 ms	604 m	A' CC=O bend
643 m	645 m	6b A' ring deformation
667 w	664 vw	4 A" ring deformation
790 m	789 w	12 A' ring deformation
825 sh		10a A" CCH bend
835 ms	836 m	17b A" CCH bend
859 m	861 m	1 A' ring deformation
946 w	947 w	17a A" CCH bend
964 w	965 w	5 A" CCH bend
1009 w	1010 w	A" H-CO wag
1014 w	1015 w	18a A' CCH bend
1113 m	1112 w	18b A' CCH bend
1140 sh		9a A' CCH bend
1161 s	1162 s	A' COH bend
1218 s	1217 m	13 A' CX stretch
1240 m	1237 w	7a A' CX stretch
1286 s	1286 m	14 A' CC stretch
1315 m	1315 m	3 A' CCH bend
1387 m	1388 w	A' O = CH bend
1452 s	1450 m	19b A' CC stretch
1519 m	1523 w	19a A' CC stretch
	1588 vs	8a A' CC stretch
1598 s	1604 vs	8b A' CC stretch
1666 s	1679 s	A' C=O stretch
2754 w	2786 w	A' H-CO stretch
3022 m	3018 w	20b A' CH stretch
3044 m	3042 w	20a A' CH stretch
	3063 w	7b A' CH stretch
	3086 w	2 A' CH stretch
	3300 broad	A" OH stretch, polymer

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

Guaiacol

Thirty of the fundamental modes of guaiacol correspond to the fundamental modes of benzene. A number of these modes are altered in the substituted

derivative; however, many are not. Characteristic numbers of such x-sensitive and x-insensitive modes have not been identified for ortho-disubstituted benzene derivatives. In their assignment of the vibrational spectra of guaiacol, Verma, Nair and Rai (108) assigned forty of the fundamental modes. Within this assignment twenty-eight of the phenyl fundamentals were assigned. Tripathi and Tripathi (109) assigned twenty-seven guaiacol fundamental modes in their study of o-substituted anisoles; nineteen of these were phenyl modes. In their study of monosubstituted phenols Green, Harrison, and Kynaston (28) assigned twenty-four guaiacol fundamental vibrations; thirteen of these were phenyl modes.

Green (28), Verma (108), and Tripathi (109) assign the phenyl modes of guaiacol by the type of mode, e.g., CC stretching or CCH bending, etc., rather than by a specific mode number. Overall, the assignments agree except for several of the substituent-sensitive modes. The in-phase and out-of-phase ring breathing modes (modes 1 and 12) and the two CX stretching modes all have differing assignments. Opposing assignments exist for the majority of the substituent modes. The assignments of the substituent modes, of modes 1 and 12, and of the CX stretching modes will be discussed in this section.

The in-phase breathing mode, vibration 1, was assigned at 832 cm^{-1} by Verma, et al. (108), and at 750 cm^{-1} by Tripathi and Tripathi (109). The out-of-phase breathing mode, vibration 12, was assigned to a shoulder at 998 cm^{-1} (108) and alternatively to an absorption band at 1028 cm^{-1} (109). In this investigation the bands for modes 1 and 12 are calculated to appear at 781 cm^{-1} and 843 cm^{-1}. They are assigned to bands at 786 cm^{-1} and 834 cm^{-1}. These assignments fall in the ranges cited for these modes by Varsanyi (6).

The C-OH stretch and the C-OCH_3 stretch were assigned to bands at 1362 and 1225 cm^{-1} by Tripathi (109). Verma (108) assigned the C-OCH_3 stretch at 1268

cm^{-1} and proposed that the C-OH stretch interacted with the OH in-plane bending mode. The resulting vibrations were assigned at 1120 and 1229 cm^{-1}. The C-OH and C-OCH_3 bond stretches arise at 1251 and 1248 cm^{-1} in phenol and anisole. In this investigation the C-OH stretch is assigned at 1223 cm^{-1} and the C-OCH_3 stretch is assigned at 1263 cm^{-1}. This assignment is based on the potential energy distribution for guaiacol. The COH and C-OCH_3 in-plane bending modes were assigned at 536 and 548 cm^{-1} by Verma (108). The corresponding out-of-plane bends were assigned to absorptions at 460 and 184 cm^{-1} (108). In this study these four modes are assigned to bands at 346, 236, 456 and 741 cm^{-1}, respectively. These assignments were made using the information available in the potential energy distribution. The last two, the out-of-plane wags of the C-OH and C-OCH_3 bonds, appear to be highly coupled to each other, with only a few percentage points distinguishing one as the C-OH wag and the other as the C-OCH_3 wag. The assignments could easily be reversed.

Three of the forty-five guaiacol fundamental modes arise from motions of the hydroxyl group: the OH stretch, the OH in-plane bend and the OH out-of-plane bend or torsion. The OH stretching and torsion modes have been included in many studies of hydrogen bonding in substituted phenols. The free OH stretch has been assigned between 3525 and 3565 cm^{-1} (28,104,108,109,115,116). The hydrogen-bonded OH stretch has been assigned at 3370 cm^{-1} (108). The OH in-plane bending mode was thought to contribute to bands at 1206 cm^{-1} and 1362 cm^{-1} (28). Paralleling this assignment in phenol, the band at 1206 cm^{-1} was assigned as mainly an OH in-plane bend, and that at 1362 cm^{-1} as principally a ring stretching band (28). Studies of the OH stretching and the OH torsion regions of the spectra of substituted phenols have suggested that in ortho-substituted phenols the hydroxyl group may exist in cis or trans orientations with respect

to the ortho position (Fig. 23). Intramolecular hydrogen bonding between the hydroxyl group and the substituent is possible in the cis-conformer. If the ortho substituent is a halogen, alkoxy, phenyl or cyano group, a second absorption band is present in the OH stretching region, except in the case of an o-methoxyl group (104). The major absorption band is attributed to the vibration of a hydroxyl group in a cis-orientation, the other to the trans-conformer. The absence of a second OH stretch in guaiacol is attributed to an unusually low intensity in the trans-isomer (104). The cis-conformer of guaiacol has been found to be the most stable, with its intramolecular hydrogen bond (117). Torsional frequencies for both the cis- and trans-forms of such ortho-substituted phenols were also observed (115). The band of greater intensity and at a higher frequency was ascribed to the cis-form. In guaiacol, the torsions for the cis- and trans-conformations were previously assigned at 428 and 388 cm^{-1}, respectively (105,115). Verma (108) assigned the free and hydrogen bonded (intermolecular) hydroxyl torsions at 308 and 681 cm^{-1}.

Cis Trans

Figure 23. The cis- and trans- orientations of the hydroxyl group.

In this investigation, the free hydroxyl stretch is found at 3556 cm^{-1} in the spectra of guaiacol. The normal coordinate calculations show this band arising at 3609 cm^{-1}. The potential energy distribution of the A' modes of

guaiacol show the band at 1208 cm^{-1} and the band at 1357 cm^{-1} to have substantial contributions from the COH bend. The 1208 cm^{-1} band is assigned as the COH bend. The 1357 cm^{-1} band is assigned as the CH bending mode corresponding to benzene mode 3. The potential energy distribution for the A" modes of guaiacol show major contributions of the hydroxyl torsion to bands calculated to occur at 356 and 286 cm^{-1}. This mode is assigned at 346 cm^{-1}.

Vibrations of the methoxyl group make up the remaining twelve guaiacol fundamental modes. As in anisole, there are three CH stretching modes (2A' + 1A"), three HCH angle deformations (2A' + 1A"), two OCH angle deformations or rocking modes (A' + A"), an in-plane COC angle bend, an O-CH_3 stretching mode and two torsions.

Green (28) assigned the symmetric and antisymmetric A' CH stretches to bands at 2958 and 3005 cm^{-1}, and the A" stretch at 2945 cm^{-1}. Alternatively, the symmetric CH stretch was attributed to a band at 2846 cm^{-1}, and the antisymmetric A" stretch at 2938 (108,109). Beckering (118) ascribed the band at 2841 cm^{-1} to the first overtone of the symmetric bending vibration, and that at 2961 cm^{-1} to an antisymmetric CH stretch.

The symmetric and antisymmetric A' and the A" HCH angle deformations were assigned at 1457, 1467 and 1443 cm^{-1}, respectively, by Green (28). Verma (108), however, assigned these modes at 1368, 1478 and 1454 cm^{-1}, and Tripathi (109) attributed the bands at 1303 and 1445 cm^{-1} to the first and last of these deformations.

Green assigned bands at 1177 and 1040 cm^{-1} to mixed CH_3 rocking and O-CH_3 stretching vibrations. Verma assigned the A' CH_3 rock to a band at 1031 cm^{-1},

and the A" CH_3 rock at 754 cm^{-1}. Tripathi attributed a band at 1110 cm^{-1} to the A' CH_3 rock. The O-CH_3 stretch was assigned at 1164 cm^{-1} (108) and 1225 cm^{-1} (109).

The in-plane COC bending mode was cited to occur at 351 cm^{-1} (108). In a study of the low frequency vibrations of guaiacol, Tylli (119) established the methyl torsion at 240 cm^{-1} in the liquid, and at 247 cm^{-1} in the solid. The methoxyl torsion was not assigned in the spectrum of the liquid. In the solid, however, it appeared at 140 cm^{-1}.

In this study the A' and A" potential energy distributions for guaiacol indicate assignments similar to those for the methoxyl modes of anisole. The symmetric, antisymmetric A' and A" CH stretching modes are assigned at 2840, 2950, and 2965 cm^{-1}, respectively. Bands at 1454, 1461, and 1443 cm^{-1} are attributed to the symmetric and antisymmetric A' and A" HCH deformations. The A' and A" rocking modes are assigned to bands at 1109 and 1155 cm^{-1}. The COC bend, the O-CH_3 stretch, the C-OCH_3 torsion and the O-CH_3 torsion are assigned to bands at 534, 1040, 108, and 236 cm^{-1}, respectively. The assignments proposed for the normal modes of guaiacol are listed in Table XXXIX.

m-Anisaldehyde

The vibrational spectra of m-anisaldehyde have been reported in the literature (110,111). The spectra have been interpreted solely by comparison to the spectra of similar molecules. Srivastava (110) proposed assignments for twenty-four of the phenyl modes, eight of the methoxyl modes, and four of the formyl modes. Dwivedi (111) suggested assignments for twenty-six of the m-anisaldehyde modes, nineteen as phenyl modes, three as formyl modes, and four as methoxyl modes.

TABLE XXXIX

ASSIGNMENT OF THE NORMAL MODES OF GUAIACOL

Infrared, cm^{-1}	Raman, cm^{-1}	Assignment
	(108)	A" C-OCH torsion
	188 m[a]	16b A" ring deformation
	236 m	9b A' CCX bend
	236 m	A" O-CH torsion
	310 m	16a A" ring deformation
	346 w	15 A' CCX bend
	346 w	A" OH torsion
	456 m	10b A" CCX bend
	502 m	6a A' ring deformation
533 m	534 m	A' COC bend
572 w	570 m	4 A" ring deformation
584 m	583 m	6b A' ring deformation
741 s	727 m	11 A" CCX bend
757 m	759 s	1 A' ring deformation
786 m		10a A" CCH bend
834 m	834 m	12 A' ring deformation
852 sh		17b A" CCH bend
917 m	913 w	17a A" CCH bend
960 w	962 w	5 A" CCH bend
1024 s	1027 s	18a A' CCH bend
1040 s	1040 m	A' O-CH stretch
1110 s	1109 w	A' methyl rock
	1134 sh	18b A' CCH bend
1156 m	1155 s	A" OCH bend
1173 m	1172 m	9a A' CCH bend
1208 m	1206 m	A' COH bend
1225 s	1223 w	13 A' CX stretch
1261 vs	1263 s	7a A' CX stretch
1303 m	1301 m	14 A' CC stretch
1361 m	1357 m	3 A' CCH bend
1444 s	1443 m	A" asym HCH bend
1458 m	1454 m	A' sym HCH bend
1463 m	1461 m	A' asym HCH bend
1470 s		19b A' CC stretch
1502 vs	1502 m	19a A' CC stretch
1597 s	1596 s	8a A' CC stretch
1615 m	1609 m	8b A' CC stretch
2843 m	2840 m	A' sym CH stretch
2950 m	2944 m	A' asym CH stretch
2965 m	2965 sh	A" asym CH stretch
	3023 w	20b A' CH stretch
3054 m	3053 sh	20a A' CH stretch
3070 w	3070 w	7b A' CH stretch
	3091 w	2 A' CH stretch
3556 m	3549 w	A' OH stretch

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

The majority of the assignments proposed by Srivastava (110) and Dwivedi (111) for m-anisaldehyde are in agreement, with the exception of the substituent sensitive phenyl modes. The assignment of the substituent sensitive phenyl modes and of the substituent modes will be discussed here.

The three modes associated with the C-OCH_3 bond, and one of the modes associated with the C-CHO bond have been assigned by Srivastava (110). The C-OCH_3 stretch, and the in-plane and out-of-plane bends were assigned at 1268, 552, and 165 cm^{-1}. He attributed the band at 866 cm^{-1} to the C-CHO stretch. Dwivedi (111) assigned the C-CHO stretch at 1190 cm^{-1}, but did not identify the C-OCH_3 stretch. He anticipated the bending modes to occur below 400 cm^{-1}, out of his range of investigation, and left them unassigned.

In benzaldehyde the C-CHO stretching mode is assigned at 1205 cm^{-1}. The potential energy distribution shows this mode contributing to several bands. Its assignment to the band at 1192 cm^{-1} is proposed in this study. This parallels Dwivedi's assignment of this mode (111). Based on the normal coordinate calculations, the C-OCH_3 stretch is assigned at 1266 cm^{-1}, in agreement with Srivastava's assignment (110). Based on the potential energy distributions the A' and A" bends of the C-OCH_3 bond are assigned at 167 and 518 cm^{-1}. The in-plane and out-of-plane bends of the C-CHO bond are assigned at 458 and 447 cm^{-1}.

Mode 1, the in-phase ring breathing mode, has been assigned at 991 cm^{-1} (110,111). The out-of-phase ring breathing mode, mode 12, was assigned to bands at 1007 cm^{-1} (110) and 790 cm^{-1} (111). Varsanyi's review of these modes in meta-disubstituted benzenes identified mode 12 to be a substituent insensitive mode, arising in the range 990-1010 cm^{-1}. Mode 1 was classified as a substituent sensitive mode, occurring between 650 and 750 cm^{-1} for light substituents

and 1050 and 1140 cm^{-1} for heavy substituents (6). Using these observations and the potential energy distribution of the A' modes of m-anisaldehyde, mode 12 is assigned at 994 cm^{-1} and mode 1 at 745 cm^{-1} in this investigation.

The vibrations of the formyl group are usually described as a CH stretch, a C=O stretch, an in-plane HCO bend, an out-of-plane hydrogen wag, and a torsion about the C-CHO bond. Four of these have been assigned in m-anisaldehyde. As in benzaldehyde, two absorption bands are observed between 2600 cm^{-1} and 2900 cm^{-1} where the aldehydic CH stretching vibration should occur, at 2834 and 2726 cm^{-1} (120). These are interpreted as resulting from a Fermi resonance interaction between the aldehydic CH stretching fundamental and the first overtone of the formyl CH bending vibration. The fundamental has previously been assigned at 2726 cm^{-1} (110,120), and at 2840 (111). A band at 1323 cm^{-1} is attributed to the in-plane HCO bend by Srivastava (110). Two solvent insensitive bands (i.e., bands that are due to the motions of atoms that are not involved in intermolecular hydrogen-bonding) are also observed in the C=O stretching region, at 1709 and 1686 cm^{-1} (107,120). Brooks (120) suggested that the band at 1686 cm^{-1} is a combination band in resonance with the carbonyl stretch at 1709 cm^{-1}. Dwivedi (111) and Srivastava (110) assigned the C=O stretch to bands at 1710 and 1704 cm^{-1}. The formyl torsion was assigned at 132 cm^{-1} (110). The out-of-plane wag of the aldehyde hydrogen was not assigned.

In this study the formyl modes are assigned based on normal coordinate calculations. The CH and C=O stretches are assigned to bands at 2731 and 1699 cm^{-1}, the in-plane CCO and HCO bends are assigned at 230 and 1385 cm^{-1}, the out-of-plane HCC bend is assigned at 1005 cm^{-1} and the torsion at 134 cm^{-1}. These assignments agree with those made by Srivastava (110) except for the assignment

of the A' HCO bend. Srivastava proposed the assignment of this bend to the 1323 cm^{-1} band, which is assigned as mode 3 in this investigation.

The methoxyl modes include three CH stretches, three HCH deformations, two OCH deformations, a $O-CH_3$ stretch, a COC A' bend, and two torsions. Srivastava (110) attributed the bands at 2827, 2945 and 2962 cm^{-1} to the symmetric and two antisymmetric CH stretching modes. Dwivedi (111) assigned these modes to bands at 2735, 2945 and 2965 cm^{-1}. The symmetric and two antisymmetric HCH bending modes were assigned to bands at 1386, 1435 and 1462 cm^{-1} (110,111). Srivastava (110) also assigned one of the OCH bends to a band at 1081 cm^{-1} and the $O-CH_3$ stretch to the band at 794 cm^{-1}.

This study supports Srivastava's assignment of the symmetric, antisymmetric A' and A" CH stretching modes to bands arising at 2827, 2945, and 2962 cm^{-1}, the antisymmetric A' HCH deformation at 1435 cm^{-1} and the A' OCH bend at 1081 cm^{-1}. However, the potential energy distribution indicates that the symmetric and antisymmetric A" HCH bends, and the $O-CH_3$ stretch should be assigned at 1460, 1436, and 1040 cm^{-1}, rather than at 1386, 1462 and 794 cm^{-1} as proposed by Srivastava (110). The potential energy distribution of m-anisaldehyde also suggests the assignment of the antisymmetric OCH deformation, the COC bend, the methyl torsions to bands at 1164, 554, and 279 (or 209) cm^{-1}. The methoxyl torsion is calculated to occur at 97 cm^{-1} but, as it is unobserved, it is unassigned in this investigation. The assignments of the normal modes of m-anisaldehyde are summarized in Table XL.

Comparison of the Normal Modes of the Disubstituted Benzenes

It is of interest, in light of the aims of this study, to look at the manner in which the assignments of the vibrational spectra of the disubstituted

TABLE XL

ASSIGNMENT OF THE NORMAL MODES OF m-ANISALDEHYDE

Infrared, cm^{-1}	Raman, cm^{-1}	Assignment
	(97)	A" C-OCH torsion
	(134)	A" CHO torsion
	167 m[a]	9b A' CCX bend
	209 m	16b A" ring deformation
	230 m	16a A" ring deformation
	230 m	A' CC=O bend
	279 m	A" O-CH torsion
447 vw	447 m	10b A" CCX bend
	456 m	15 A' CCX bend
470 vw	470 sh	6a A' ring deformation
518 vw		11 A" CCX bend
554 m	554 m	A' COC bend
647 m	648 m	6b A' ring deformation
683 s	684 w	4 A" ring deformation
738 s	738 m	1 A' ring deformation
789 s	788 w	10a A" CCH bend
868 m	871 w	17b A" CCH bend
901 m	901 w	17a A" CCH bend
952 w	952 w	5 A" CCH bend
981 w	983 m	18a A' CCH bend
993 m	994 vs	12 A' ring deformation
1005 w	1002 w	A" H-CO wag
1040 s	1037 m	A' O-CH stretch
1079 w	1079 m	18b A' CCH bend
	1087 w	A' methyl rock
1149 s	1149 m	9a A' CCH bend
1165 m	1164 m	A" methyl rock
1192 m	1191 m	13 A' CX stretch
1266 vs	1262 s	7a A' CX stretch
1286 s	1285 m	14 A' CC stretch
1324 m	1324 m	3 A' CCH bend
1385 m	1384 w	A' HC=O bend
	1435 m	A" asym HCH bend
1436 m		A' sym HCH bend
1460 s	1457 m	A' asym HCH bend
1466 s	1464 w	19b A' CC stretch
1486 s	1484 m	19a A' CC stretch
1587 s	1589 s	8a A' CC stretch
1597 s	1599 s	8b A' CC stretch
1703 vs	1699 s	A' C=O stretch
2731 m	2725 w	A' H-CO stretch
2840 m	2835 m	A' sym CH stretch
2943 m	2941 w	A' asym CH stretch
2964 m	2963 vw	A" asym CH stretch
3035 m		20b A' CH stretch
	3053 w	20a A' CH stretch
3064 w	3060 sh	7b A' CH stretch
3071 w	3070 m	2 A' CH stretch

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

benzenes compare to each other and to the appropriate monosubstituted benzenes. Knowledge of the behavior of both the phenyl modes and the substituent modes on changing the extent or pattern of substitution of the aromatic ring will aid in the interpretation of the vibrational spectra of lignins.

Frequencies

Comparison of the observed vibrational spectra of the disubstituted spectra to those of the appropriate monosubstituted compounds elucidates the reaction of the phenyl and substituent modes to disubstitution. In general, it appears that in addition to the three phenyl modes associated with the additional CX bond, the frequencies of three other phenyl modes are influenced by disubstitution. The majority of the substituent modes are found to be relatively unaffected by further substitution on the ring.

The wavenumbers of benzene and the phenyl modes of the monosubstituted and disubstituted benzenes are presented in Table XLI. Comparisons of the spectra of the disubstituted compounds to the spectra of the appropriate monosubstituted benzenes are presented in Fig. 24-26. The dashed lines connect the phenyl bands. As expected, the vibrations involving the CX bonds undergo the largest shifts. These include the two CX stretches, the two in-plane CX bends and the two out-of-plane CX bends which are derived from phenyl modes 7a, 13, 9b, 15, 10b and 11, respectively. Modes 1, 6a and 16b, identified to be substituent sensitive on monosubstitution, continue to be substituent sensitive on disubstitution. Substituent sensitive modes unique to the disubstituted compounds include vibrations 12, 6b and 16a. Modes 1, 6a, 12 and 6b are in-plane ring deformation modes. Modes 16a and 16b are out-of-plane ring deformation modes. Mode 16a is not identified as substituent sensitive in the literature review of the spectral assignments for disubstituted benzenes. However, it appears to be

so in the proposed assignments of these compounds. The remainder of the phenyl modes are relatively stable to disubstitution.

TABLE XLI

WAVENUMBERS (CM^{-1}) OF THE BENZENE MODES AND THE PHENYL MODES OF MONO- AND DISUBSTITUTED BENZENES

Mode	Benzene	Phenol	Benz-aldehyde	Anisole	4-Hydroxy-benzaldehyde	Guaiacol	m-Anis-aldehyde
				In-plane Modes			
2	3064	3087	3088	3093	3086	3091	3071
7b	3055	3076	3065	3069	3063	3070	3060
20a	3055	3061	3045	3055	3042	3054	3056
20b	3043	3046	3035	3037	3022	3023	3035
8b	1594	1605	1600	1600	1598	1615	1599
8a	1594	1595	1588	1587	1588	1596	1589
19a	1483	1499	1496	1497	1519	1502	1486
19b	1483	1471	1458	1455	1450	1470	1466
3	1348	1388	1314	1336	1315	1357	1324
14	1309	1345	1288	1304	1286	1301	1286
13*	3037	1251	1205	1248	1240	1263	1266
7a*	3043	3022	3026	3033	1218	1223	1192
15*	1149	1152	1162	1172	451	534	458
9a	1179	1168	1168	1181	1140	1172	1149
18b	1039	1071	1072	1078	1112	1134	1079
18a	1039	1024	1023	1021	1015	1027	983
12*	1012	1000	1002	995	789	834	994
1*	999	812	830	784	861	786	745
6b*	608	618	615	615	645	583	647
6a*	608	530	439	443	402	502	470
9b*	1179	416	226	266	222	236	167
				Out-of-Plane Modes			
5	990	986	989	975	964	962	952
17a	968	958	962	960	947	917	901
17b	968	890	924	885	835	852	868
10a	850	818	851	820	825	759	788
10b*	850	509	451	513	507	456	447
4	704	690	689	692	667	570	684
11*	672	756	746	757	349	741	518
16a*	404	416	410	415	415	310	230
16b*	404	242	237	214	179	188	209

*Substituent sensitive modes.

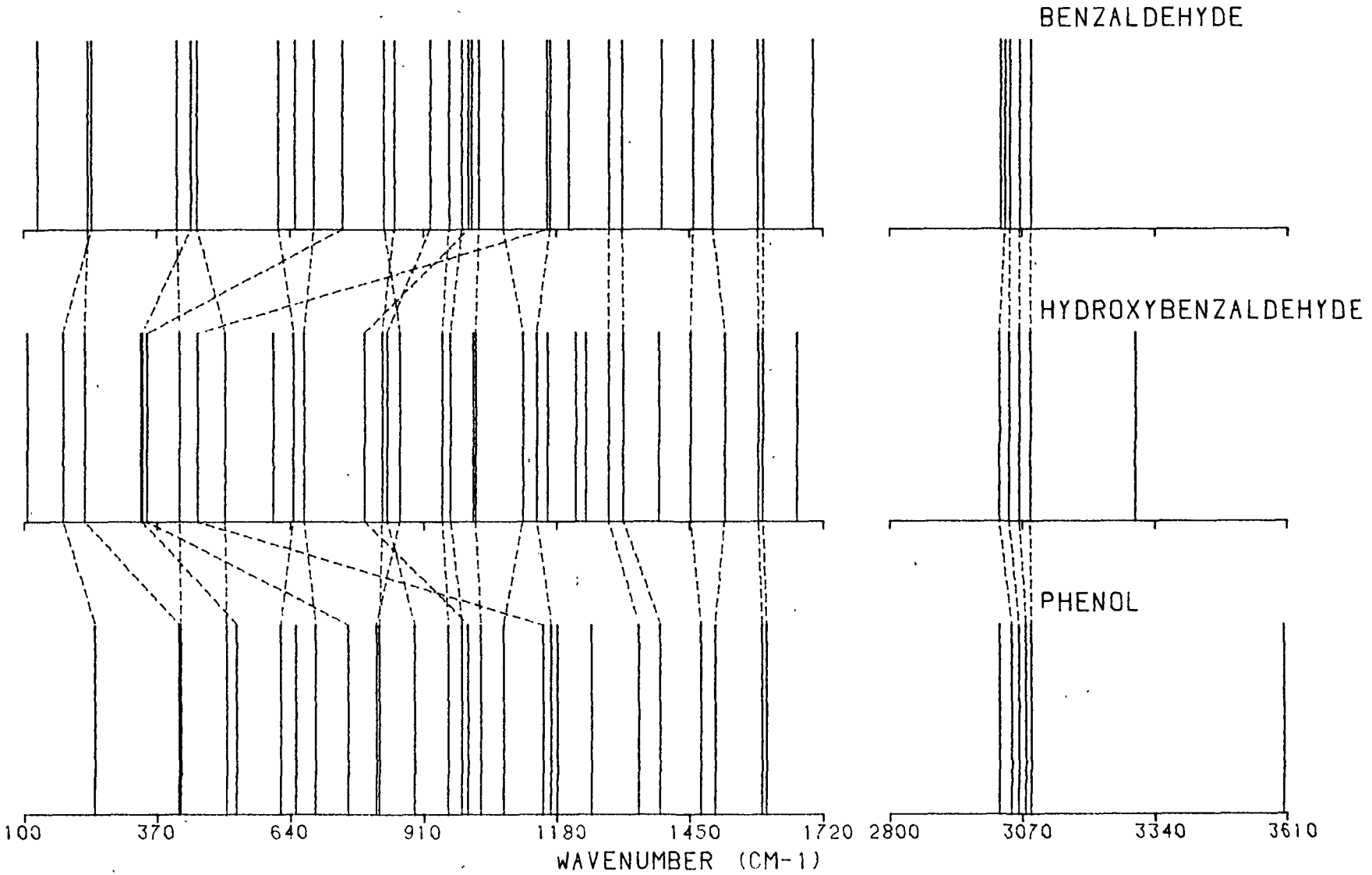


Figure 24. Comparison of the phenyl modes of mono- and disubstituted benzenes, 4-hydroxybenzaldehyde compared to phenol and benzaldehyde. The dashed lines connect the phenyl modes.

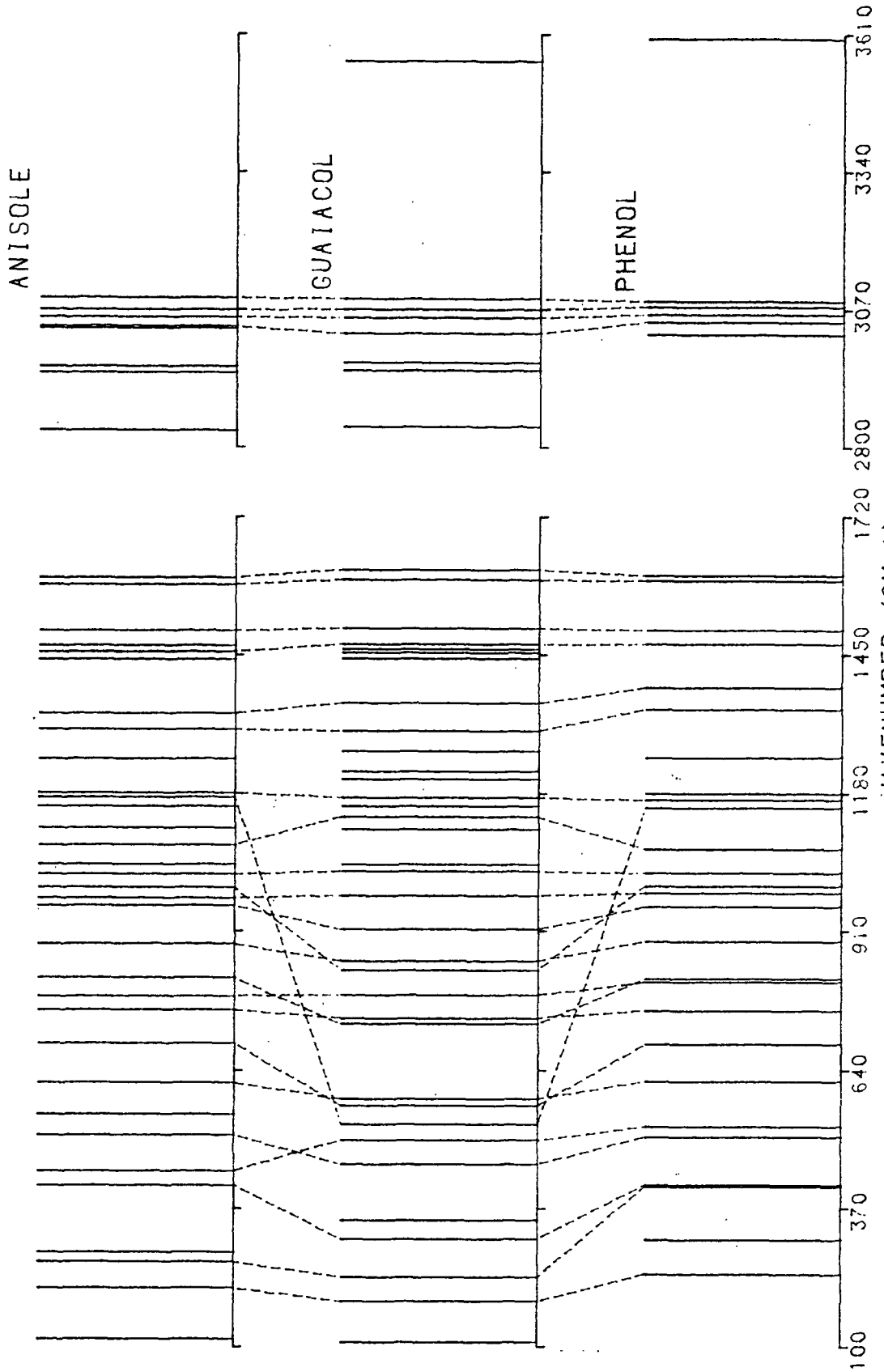


Figure 25. Comparison of the phenyl modes of mono- and disubstituted benzenes, guaiacol compared to phenol and anisole. The dashed lines connect the phenyl modes.

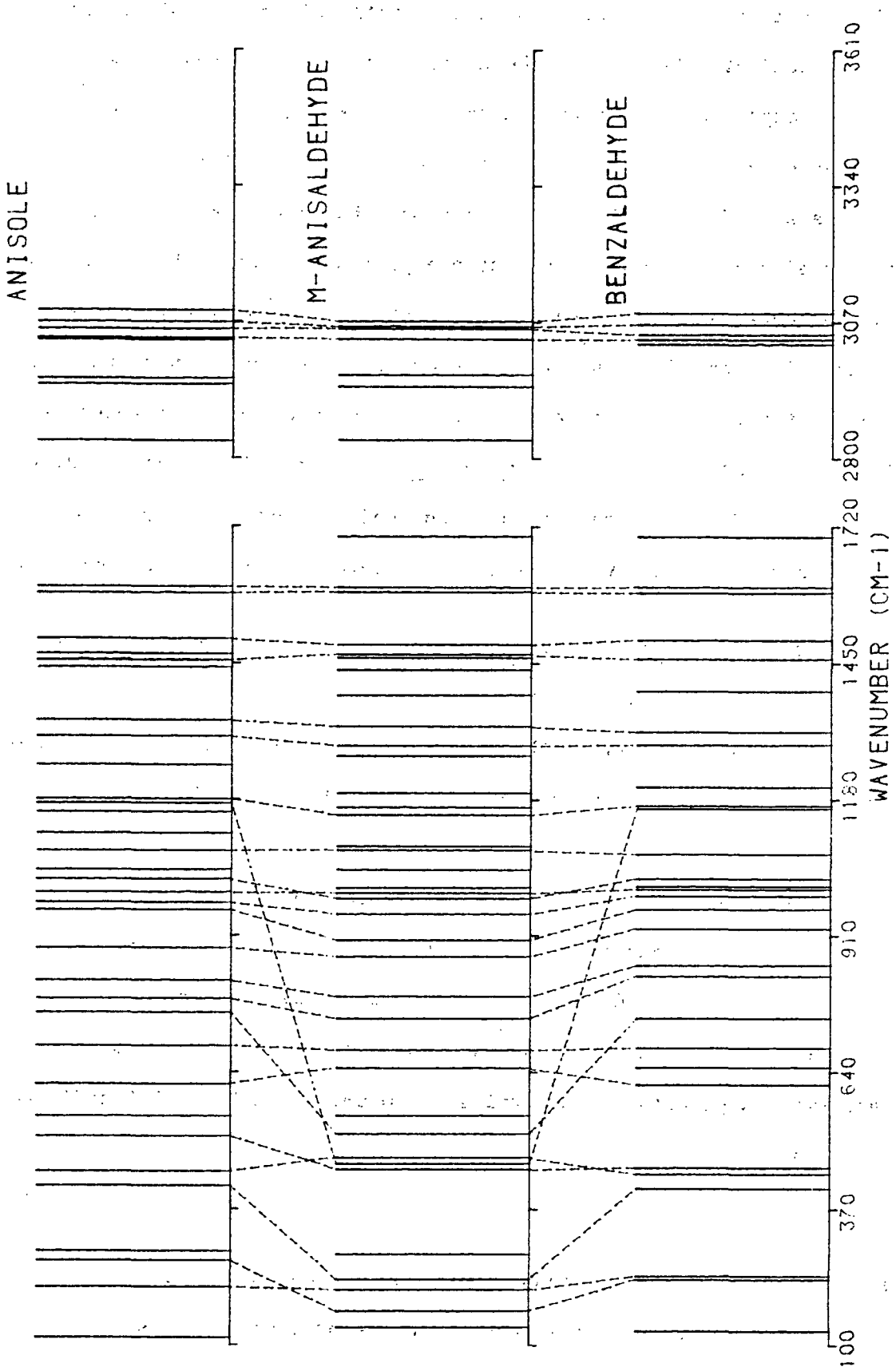


Figure 26. Comparison of the phenyl modes of mono- and disubstituted benzenes, m-anisaldehyde compared to benzaldehyde and anisole. The dashed lines connect the phenyl modes.

Figure 27 is a line representation of the vibrational spectra of benzene and the three disubstituted benzenes. The dashed lines connect the bands arising from the phenyl modes. Comparison to a similar figure for the monosubstituted benzenes (Fig. 13) emphasizes the fact that the positions of the phenyl modes are also influenced by the pattern of substitution on the ring. Both on mono- and disubstitution many of the phenyl bands shift. The positions of these bands in monosubstituted benzenes are little affected by varying the substituent. Changing one of the substituents and the pattern of substitution, however, has a greater effect on the phenyl modes of disubstituted benzenes, as is seen in Fig. 27. Analysis of the o-, m- and p- versions of each of the disubstituted compounds would be necessary to sort out which effects were due to the change in substituents and which were due to the change in substitution pattern.

The wavenumbers of the modes arising from the substituent groups are presented in Table XLII. Inspection of this table reveals that the substituent modes are relatively unaffected by further substitution on the ring. The potential energy distributions of the two modes that are shifted, the formyl A' HCC bend and the methoxyl A' COC bend show them to be coupled with both phenyl and other substituent modes; their assignments could be changed. The only other assignments that require comment are those of the OCH bend and O-CH_3 stretch in guaiacol. The potential energy distributions for these frequencies support the assignment shown in Table XXXIX. The intensities of the bands however support reversing these two assignments and assigning the O-CH_3 stretch at 1040 cm^{-1} and the OCH deformation at 1109 cm^{-1}.

Intensities

A comparison of the relative intensities of the IR and Raman bands of the phenyl modes of disubstituted benzenes reveals few recognizable trends. The

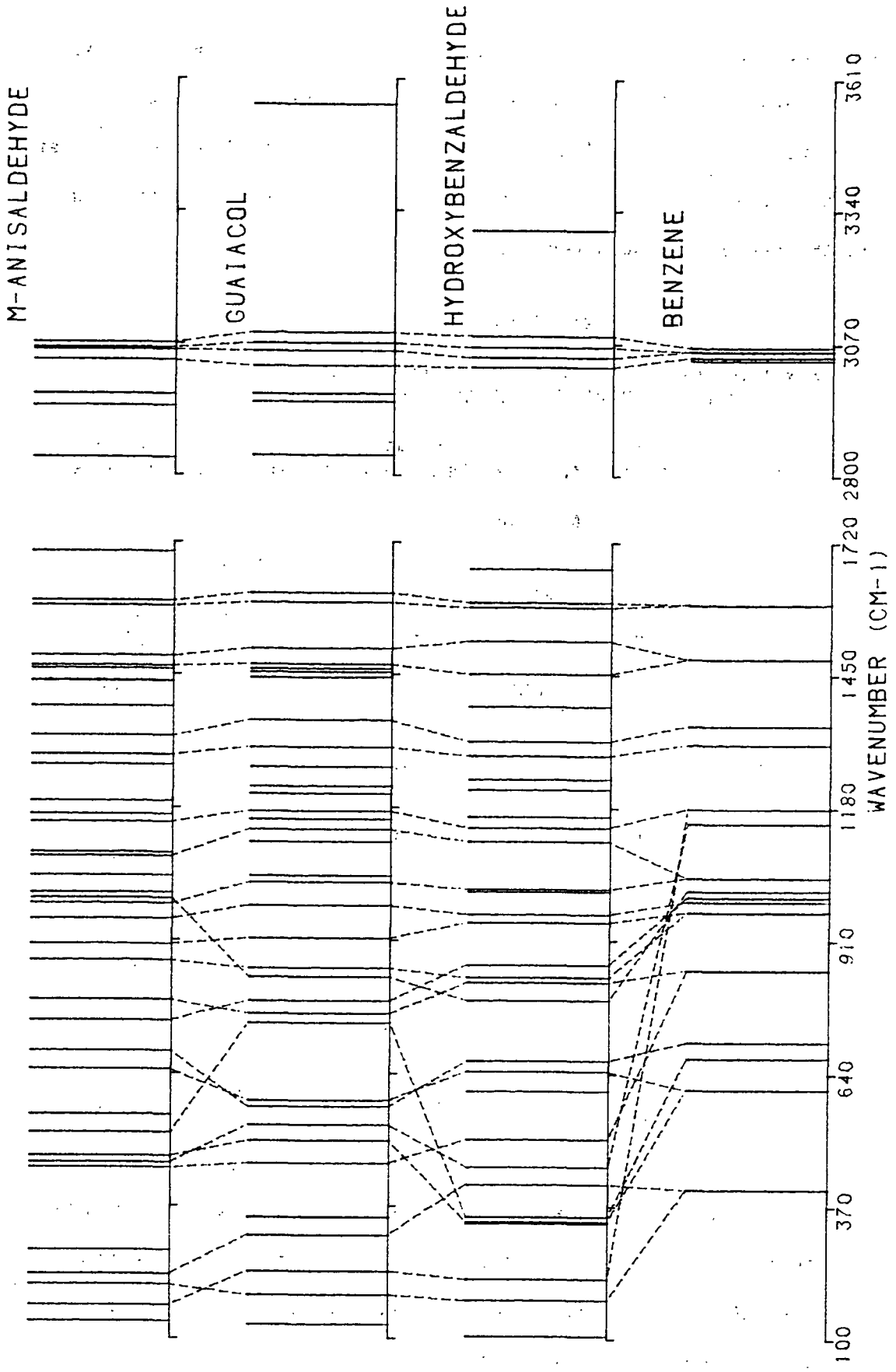


Figure 27. Comparison of the phenyl modes of the disubstituted benzenes. The dashed lines connect the phenyl modes.

intensities of these bands are affected by both the nature of the substituents and the pattern of substitution. The relative intensities of the substituent bands in the spectra of the disubstituted compounds are less influenced by other substituents on the ring, most having the same intensity in the disubstituted compounds as in the monosubstituted benzenes.

TABLE XLII

WAVENUMBERS (CM^{-1}) OF THE SUBSTITUENT MODES OF MONO- AND DISUBSTITUTED BENZENES

Mode	Phenol	Benz-aldehyde	Anisole	4-Hydroxy-benzaldehyde	Guaiacol	m-Anis-aldehyde
			A' Modes			
OH stretch	3602			(3300)	3556	
CH stretch			2945		2950	2942
CH stretch			2833		2840	2844
CH stretch		2737		2754		2731
C=O stretch		1700		1679		1669
HCH bend			1468		1461	1460
HCH bend			1441		1454	1435
O=CH bend		1394		1387		1385
COH bend	1180			1162	1208	
OCH bend			1112		1040	1087
O-CH_3 stretch			1040		1109	1040
HCC bend		649		604		230
COC bend			553		346	554
			A" Modes			
CH stretch			2957		2965	2964
HCH bend			1456		1443	1436
OCH bend			1154		1155	1164
CH wag		1008		1010		1005
OH torsion	309			337	346	
O-CH_3 torsion			(285)		236	279
CHO torsion		128		106		134
C-OCH_3 torsion			(115)		108	(97)

A few generalities can be drawn about the relative intensities of the phenyl modes of disubstituted benzenes. The CH stretching modes are of weak to medium intensity in both the IR and Raman spectra. The bands of the ring stretching modes, 19a, 19b and 14, tend to be medium to strong in the IR spectra and medium

to weak in the Raman effect. The other two ring stretching modes, 8a and 8b, have bands of medium to strong intensity in both the IR and Raman spectra. The IR intensity of the higher frequency band of this pair is known to be affected by the nature and positions of the substituents (6). In this mode, the opposite ends of the molecule (e.g., carbons 1 and 4) move away from and toward each other, in-phase. If the substituents are the same, as in benzene, there is no change in the overall dipole moment during the vibration and the band does not appear in the IR spectrum. In p-disubstitution with one electron-donor and one electron-acceptor, as in 4-hydroxybenzaldehyde, there is a large change in the dipole moment resulting in a strong IR band. In m- and o-disubstitution the nature of the substituents still affect the intensity of the IR band but in a less predictable manner (82). The lower frequency band of this pair is generally more intense in the Raman effect. Vibration 3 is found with medium intensity in both the IR and Raman spectra of all three compounds. The intensity of the CX stretching modes vary with the nature of the substituent. If X = OH or OCH_3, the bands are strong in the IR. If X = CHO the band is not as intense. The Raman bands are generally less intense than their IR counterparts. The remainder of the in-plane modes have medium to weak intensity in both the IR and Raman spectra with no discernible pattern to their variation. The intensities of the individual bands can be rationalized to some extent by consideration of the form of the mode and the nature of the substituents. Only the intensities of the CH, CC and CX stretching modes show the same trends in both the mono- and disubstituted benzenes. The intensities for these modes in monosubstituted benzenes are the same as they are for disubstituted benzenes. As there is no trend to the variation in intensity of the remaining modes in disubstituted benzenes, no trend is observed in these modes when comparing their intensities in the mono- and disubstituted compounds.

The Raman bands of the A" modes of the disubstituted benzenes are of medium to weak intensity. With the exception of the characteristic CH out-of-plane bending modes, the IR bands of these modes are also of medium to weak intensity. There is no apparent pattern to the changes in intensity between compounds. The characteristic CH out-of-plane bending modes give rise to bands of strong intensity in IR spectra. Their position is determined principally by the positions of the substituents, not their chemical nature (82). In o-disubstituted compounds a strong band is expected between 770 and 735 cm^{-1}. This band occurs at 741 cm^{-1} in guaiacol. Strong bands are expected in the ranges 810-750 cm^{-1} and 860-800 cm^{-1} for m- and p-disubstitution, respectively. These bands are assigned at 788 cm^{-1} in m-anisaldehyde and 835 cm^{-1} in 4-hydroxybenzaldehyde.

The intensities of the A" modes of disubstituted benzenes are similar to those of the monosubstituted benzenes. The Raman bands of the A" modes of monosubstituted benzenes are of medium to weak intensity. With the exception of the characteristic CH out-of-plane bending modes, the IR bands of the A" modes are also of medium to weak intensity.

The majority of the substituent modes are found to have the same IR intensities in the disubstituted compounds as in the monosubstituted benzenes. The intensities of their Raman bands are more variable. The stretches of the C-O and C=O bonds have strong IR and Raman bands in all spectra. The CH and OH stretches are of medium IR intensity and are medium to weak in the Raman effect. The HCH and OCH bends of the methoxyl group have medium to strong intensity in the IR and medium-weak intensity in the Raman spectra. The COC bend of the methoxyl group has a medium to weak intensity band in both the IR and Raman spectra. The COH bend of the hydroxyl and formyl groups has strong IR bands and variable intensity Raman bands.

SUMMARY

Normal coordinate analyses were performed for the disubstituted benzenes using force constants transferred from the modified valence force fields developed for the monosubstituted compounds. The results of these calculations and group frequency data were used to assign the vibrational spectra of 4-hydroxybenzaldehyde, m-anisaldehyde, and guaiacol. These assignments were compared with the assignments proposed for the monosubstituted benzenes to ascertain the effect of a second substituent on the frequencies and intensities of the fundamental modes of the aromatic ring. The frequencies and intensities of the fundamental modes of the substituent vibrations of the disubstituted compounds were also compared to each other and to the appropriate monosubstituted benzene derivatives.

The assignments of the vibrational spectra of the disubstituted benzenes agreed, in general, with previous assignments. New assignments were proposed for several of the fundamentals. Assignments were also suggested for several previously unassigned bands. Comparison of the vibrational spectra of the substituted benzenes revealed the frequencies of twelve of the phenyl modes to be sensitive to disubstitution. Six of these modes are associated with the two CX bonds, and six are in-plane and out-of-plane ring deformation modes. The frequencies of the remaining eighteen phenyl modes were classified as substituent insensitive. The frequencies of the substitutent modes were also largely insensitive to other substituents on the ring.

The intensities of the IR and Raman bands of the phenyl modes of disubstituted benzenes are influenced by both the nature of the substituents, the pattern of substitution, and the form of the mode. The bands arising from the CC

stretching modes of the ring, and one of the in-plane CCH bends are the only bands having the same relative intensities in the spectra of all three disubstituted compounds. The intensities of the other phenyl modes vary as the pattern of substitution and the nature of the substituents vary, and can be rationalized based on these changes. Most of the substituent modes were found to have the same IR intensities in the disubstituted compounds as in the monosubstituted benzenes. The intensities of the Raman bands were more variable.

CHAPTER IV. ANALYSIS OF THE VIBRATIONAL SPECTRA OF THE TRISUBSTITUTED BENZENE: VANILLIN

INTRODUCTION

The vibrational spectra of vanillin are interpreted using normal coordinate analysis, group frequency data and information elicted from the vibrational spectra. The IR and Raman spectra of solid vanillin and of solutions of vanillin were recorded. Normal coordinate calculations are performed using a modified valence force field. The force constants for this field are transferred from the MVFF's developed for the monosubstituted benzenes Chapter II. The distribution calculated with this force field is used to assign the spectra of vanillin. This assignment is compared to those of the mono- and disubstituted benzenes to ascertain the effect of trisubstitution on the phenyl modes.

The normal coordinate calculations and band assignments for vanillin are presented in this section. The literature on the assignments of the vibrational spectra of vanillin and of trisubstituted benzenes is briefly reviewed. The construction of the kinetic and potential energy matrices is detailed. The assignments of the phenyl and substituent modes of vanillin and the effect of trisubstitution of the ring on the phenyl modes are discussed.

LITERATURE REVIEW

Previous assignments of asymmetric trisubstituted benzenes in general, and of vanillin in particular, are briefly reviewed. The details of these assignments are presented and are compared to the assignments proposed in this investigation in the section discussing the proposed spectral assignments.

TRISUBSTITUTED BENZENE DERIVATIVES

Trisubstitution on benzene may be symmetric (1,3,5-trisubstituted), vicinal (1,2,3-trisubstituted) or asymmetric (1,2,4-trisubstituted). The symmetry of a trisubstituted benzene depends on the pattern of substitution and the structure of the substituents. Asymmetric trisubstituted benzenes, such as vanillin, have C_s symmetry at best. Under this point group the thirty benzene fundamental vibrations divide into twenty-one A' and nine A" vibrations.

These benzene modes can be divided into substituent sensitive and substituent insensitive modes. The number of substituent sensitive modes increases as the extent of substitution increases, but a unique number of such modes has not been identified for trisubstituted benzenes. The pattern of trisubstitution as well as the mass and nature of the substituents determine the frequencies of the phenyl modes.

Relative to the vast amount of information available on mono- and disubstituted benzenes, little is known about trisubstituted benzenes. Varsanyi (6) and Bellamy (82) both review the effect of trisubstitution of benzene on the fundamental modes of benzene. Their observations, as they pertain to vanillin, are briefly discussed here. A more detailed discussion is included in Appendix II.

On trisubstitution of the aromatic ring, three of the hydrogen atoms are replaced by substituents. Therefore, three each of the six CH stretching modes, the six CH in-plane bending modes and the six CH out-of-plane bending modes will be x-sensitive modes. The remaining CH modes are relatively unaffected by substitution of the ring.

In vanillin, the three CX stretching modes, modes 7a, 7b and 13 should appear in the ranges: 1100-1210 cm^{-1}, 300-460 cm^{-1}, and 250-400 cm^{-1}, respectively. The frequency intervals of the three CX in-plane bending modes, 9a, 9b and 18a, overlap considerably. The frequency range for all three vibrations extends from 190-390 cm^{-1}. Modes 5, 17a and 17b are the CX out-of-plane bending modes for vanillin. These three modes should arise in the ranges 190-270 cm^{-1}, 140-170 cm^{-1} and 160-240 cm^{-1}, respectively.

The in-plane ring deformations, vibrations 1, 12, 6a and 6b are all sensitive to trisubstitution to varying degrees. Their frequencies are influenced by the pattern of substituents and the masses of the substituents (whether heavy, > 25 amu or light, < 25 amu). In vanillin, the substitution pattern is such that modes 1, 12, 6a and 6b should occur in the ranges 600-750 cm^{-1}, > 1000 cm^{-1}, 600-750 cm^{-1}, and 660-850 cm^{-1}, respectively.

The five CC stretching modes of the phenyl ring are all considered to be x-insensitive. As well, the three out-of-plane ring deformations are thought to be relatively insensitive to trisubstitution. The frequency ranges for these modes, and the other phenyl modes of trisubstituted benzenes are presented in Table XLIII.

VANILLIN

Vanillin is a member of the C_s point group if it is assumed to have a plane of symmetry coincident with the aromatic ring. Due to this plane of symmetry the fifty-one fundamental modes of vanillin divide into thirty-four A' and seventeen A" modes. All of these modes are both IR and Raman active. The substituent modes of vanillin have been assigned in studies of the various substituent groups. Tariq, Verma and Aquell (121) proposed assignments of the

TABLE XLIII

FREQUENCY RANGES FOR TRISUBSTITUTED BENZENES

	Wavenumber, cm^{-1}
CH stretching modes	
2, 20a, 20b	3000-3120
CC stretching modes	
8a	1560-1610
8b	1571-1642
14	1240-1290
19a	1370-1450
19b	1460-1530
CH in-plane bending modes	
3	1260-1305
9a	1140-1170
18b	1070-1120
In-plane ring deformations	
1 1,1,1; h,h,l[a]	500-600; 600-750
6a 1,1,1; h,h,l	450-540; 600-750
6b 1,1,1; h,h,l	420-480; 660-850
12 1,1,1; h,h,l	700-840; < 600
CH out-of-plane bending modes	
5	920-970
11	800-860
17b	860-900
Out-of-plane ring deformations	
4, 16a, 16b	420-600
X-sensitive modes	
9a CX in-plane bend, 9b CX in-plane bend, 18a CX in-plane bend	190-390
7a CX stretch 1,1,1; h,h,h	1240-1310; 300-460
7b CX stretch 1,1,1; h,h,h	880-970; 250-400
13 CX stretch 1,1,1; h,h,h	1100-1210; 350-580
10a CX wag 1,1,1; h,h,h	190-270; 200-310
10b CX wag 1,1,1; h,h,h	140-170; 90-130
17a CX wag 1,1,1; h,h,h	160-240; 150-190

[a] l, substituent < 25 amu; h, substituent > 25 amu.

IR and Raman spectra of vanillin based on group frequency information. General assignments were presented for the phenyl modes (i.e., CC stretch, CH bend, etc.). They also assigned the six formyl and the three hydroxyl modes and ten of the twelve methoxyl modes.

EXPERIMENTAL

SAMPLE PREPARATION

Vanillin from other research efforts at IPC was available for use. This was purified by recrystallization from water (112). The resulting crystals were dried over P_2O_5, under vacuum. The melting point of this recrystallized product was 81°C, which matches the literature value of 81-82°C (113). The infrared spectrum of this solid duplicated that reported by Sadtler (61).

MEASUREMENT OF SPECTRA

The IR spectrum of vanillin was taken of the solid as a KBr pellet. IR spectra of vanillin in carbon tetrachloride and carbon disulfide solutions were also recorded. The Raman spectra of vanillin as a solid and in carbon tetrachloride and aqueous solutions were measured. Instrumentation was as specified for the mono- and disubstituted benzene derivatives (Table VII).

EXPERIMENTAL RESULTS

The vibrational spectra of vanillin are presented in Fig. 28. The positions of the bands are tabulated in Table XLIV. The Raman and infrared solution spectra of vanillin are presented in Appendix III. As in the mono- and disubstituted benzenes, the principal features of the spectra recorded for the dilute solutions of these compounds are similar to those of the spectra of the pure

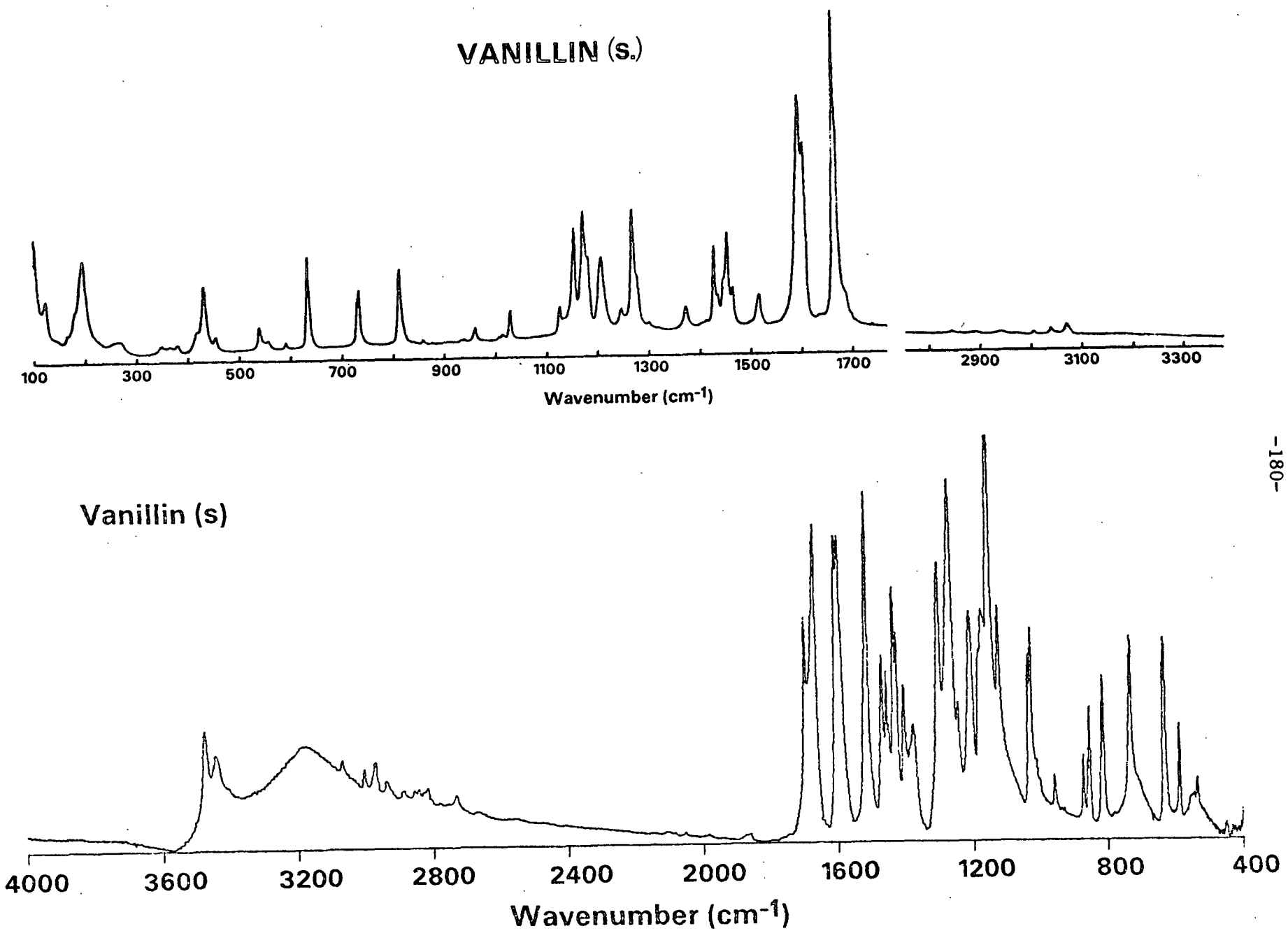


Figure 28. The Raman (upper) and infrared (lower) spectra of vanillin.

TABLE XLIV

SPECTRAL DATA - VANILLIN (SOLID)

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	122 s[a]	1208 s	1206 m
	141 s	1245 m	1245 m
	166 w	1269 vs	1267 s
	195 s	1301 s	1301 w
	257 w	1378 m	1371 m
	265 w	1406 m	1403 w
	345 w		1412 w
	363 w	1428 s	1426 m
	378 w	1437 s	1434 m
	416 w		1441 sh
	429 m	1451 m	1453 s
450 w	452 w	1458 m	
500 w		1472 m	1464 m
537 m	538 m		1499 w
548 m		1515 vs	1515 m
556 w	555 w		1549 sh
588 m	588 w	1596 s	1593 s
610 w		1605 s	1603 s
635 s	632 w	1669 s	1664 vs
666 w			1687 sh
734 s	732 m	1698 s	1701 sh
781 w			1706 sh
815 m	812 m	2576 vw	2583 vw
855 m	857 w	2668 vw	2665 vw
861 m		2712 vw	
875 m	874 w	2732 w	2733 w
888 vw	887 w	2751 vw	2754 vw
	908 w		2770 vw
931 w	931 w	2782 vw	2784 vw
937 w	937 w		2794 vw
960 m	960 w	2819 w	2815 vw
	1005 w	2826 vw	2830 vw
	1013 w	2845 w	2843 w
1030 s	1029 m	2857 w	
1036 m		2888 w	2888 w
	1078 sh		2918 w
	1095 sh	2939 w	2938 w
1123 s	1124 m	2972 m	2969 w
	1136 sh	3005 m	3004 w
1150 vs	1154 s	3040 vw	3040 w
1165 sh			3048 m
1173 s	1172 s	3070 m	3070 m
1183 m	1180 sh	3186 m	3183 w
			3535 w
		3443 m	
		3475 ms	
			3611 vw

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

compounds. The main differences are due to changes in the hydrogen bonding of the compound.

VIBRATIONAL ANALYSIS

The force fields developed for the monosubstituted benzenes are used to calculate the frequencies of the normal modes of the trisubstituted benzene under investigation. As for the disubstituted benzenes, both the kinetic and potential energy matrices for vanillin are constructed using parameters developed for the monosubstituted compounds.

KINETIC ENERGY MATRIX

The kinetic energy matrix for vanillin is calculated using the molecular geometries and internal coordinate used to define the monosubstituted compounds.

Molecular Structure

The geometry used for vanillin is a composite of the structures used for phenol, benzaldehyde and anisole. The standard ring geometry is coupled with the structural parameters of the hydroxyl, formyl and methoxyl groups. The parameters used are listed in Table XI. Vanillin is assumed to be planar. No experimentally determined structure for vanillin was found in the literature.

Internal Coordinates

A set of sixty-six internal coordinates is used to describe the normal modes of vanillin. This set includes twenty-one coordinates for the in-plane modes of the aromatic ring: six CC stretches, three CH stretches, six CCH bends and six CCC bends. And nine coordinates for the out-of-plane modes of the phenyl group: six torsions and three CH wags. It also contains eight in-plane and

four out-of-plane coordinates for the formyl group, five in-plane and two out-of-plane coordinates for the hydroxyl group, and seventeen coordinates for the methoxyl group. The substituent coordinates are defined as they were for the monosubstituted compounds. This set of internal coordinates includes fifteen redundant coordinates. Six of these redundancies are a result of the cyclical structure. The remaining redundancies are due to the overdefinition of the angles about the carbon atoms in the molecule. The internal coordinate definitions for vanillin are listed in Appendix IV.

POTENTIAL ENERGY MATRIX

A modified valence force field is used to calculate the normal modes of vanillin. The eighty-six parameter MVFF for vanillin is a composite of the force fields developed for phenol, benzaldehyde and anisole. This force field comprises twelve valence force constants for the in-plane and eight force constants for the out-of-plane modes of the phenyl group, fifteen force constants for the in-plane and seven force constants for the out-of-plane modes of the C-CHO group, twelve force constants for the in-plane and five force constants for the out-of-plane modes of the C-OH group, and twenty-seven force constants for the vibrations of the $C-OCH_3$ group. The substituent portions of this force field are transferred directly from the monosubstituted benzene force fields. No additional force constants are included to account for interactions between substituent groups. Two sets of values were used for the phenyl force constants. One was developed by the refinement of the phenyl force constants over the frequencies of all three monosubstituted benzenes. The other was developed by a similar refinement over the frequencies of all three disubstituted benzenes. The values of the substituent force constants were taken from the results of the substituent refinements of the monosubstituted compounds.

CALCULATIONS

The kinetic and potential energy matrices are used to calculate the frequencies of the fundamental modes of vanillin. The results of this calculation are used to assign the IR and Raman spectra of vanillin. Based on these assignments, the thirty-four A' modes are calculated with an average error of 13.62 cm^{-1} or 1.622%, using the monosubstituted phenyl force constant values. The seventeen A" modes are calculated with an average error of 10.44 cm^{-1} or 2.281% using force constants from the monosubstituted force field refinements. The fit does not significantly change if the phenyl force constants from the disubstituted refinement are used, e.g., the A' modes are calculated with an average error of 14.08 cm^{-1} or 1.647%. The observed and calculated frequencies and the potential energy distributions for vanillin are listed in Tables XLV and XLVI. The accuracy of fit of the calculated frequencies to the observed frequencies can be seen when the line representaions of the calculated and observed spectra are compared (Fig. 29). No particular pattern in the errors of the calculated wavenumbers of vanallin is noted when they are compared to those of the monosubstituted benzenes.

INTERPRETATION OF SPECTRA

The vibrational spectra of vanillin are assigned using the results of the normal coordinate calculations. The assignments of the normal modes of the phenyl, hydroxyl, formyl and methoxyl groups in the mono-, di-, and trisubstituted benzenes are compared. The spectral assignment and the comparisons of the normal modes of vanillin are discussed in this section.

Spectral Assignments

The IR and Raman spectra are assigned using the potential energy distribution calculated from the MVFF discussed above as well as spectral information.

TABLE XLV

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE A' VIBRATIONS OF VANILLIN

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
3538	3609	-71	-2.02	OH P(100)
3070	3074	-4	-0.12	CH(98)
3052	3056	-4	-0.14	CH(99)
3040	3039	1	0.04	CH(100)
2942	2951	-9	-0.31	CH M(99)
2844	2835	9	0.33	CH M(100)
2733	2739	-6	-0.21	CH B(98)
1698	1697	1	0.04	CO B(69) OCHB(21)
1605	1647	-42	-2.64	CC(72) CCH(14) CCC(11)
1596	1607	-11	-0.72	CC(76)
1515	1512	3	0.19	CCH(40) CC(39)
1464	1465	-1	-0.09	OCHM(60) HCHM(37)
1453	1461	-8	-0.56	CC(37) CCH(22)
1426	1443	-17	-1.20	HCHM(77) OCHM(18)
1399	1390	9	0.62	OCHB(49) CO B(22) CC(9)
1371	1346	25	1.80	CC(72) CCH(37) COHP(20)
1301	1301	0	-0.00	CC(53) CCH(46)
1267	1299	-32	-2.51	CCC(23) CO M(23) COHP(13)
1208	1229	-21	-1.70	CO P(31) CC(27) CCH(15) CO M(10)
1173	1176	-3	-0.24	COHP(34) CC(28) CCH(22) CC B(12) CO P(12)
1150	1159	-9	-0.78	OCHM(17) CC(16) CC B(14) COHP(13) CCH(12) OC M(11) CO M(10)
1124	1135	-11	-1.01	CCH(47) CC(27)
1112	1115	-3	-0.25	OCHM(58) HCHM(11) CCH(10) CC(10)
1030	1043	-13	-1.24	OC M(54) CC(21) CCH(11)
960	974	-14	-1.44	CC(30) CO M(14) CC B(12)
855	849	6	0.73	CC(27) CCC(18) CO P(16)
732	740	-8	-1.10	CCC(28) CC(14) CCOB(14) CO M(10)
632	622	10	1.60	CC(15) CCOP(14) COCM(13)
588	573	15	2.51	CCC(26) CC(19) CCOB(12)
538	514	24	4.50	CCC(22) CCOP(15) CO M(13) CC(10)
429	423	6	1.41	CCC(22) CCCB(18) COCM(14) CCOP(10) CC B(10)
363	330	33	9.17	CCOP(40) CC(11) CCC(11)
257	227	30	11.72	CCCB(30) CCOB(24) CCOM(21) COCM(19) CCOP(11)
141	144	-3	-2.19	CCOM(49) COCM(35) CCCB(22) CCOB(10)
Average Error		14	1.62	

[a]The internal coordinates are the phenyl CC stretches (CC), CH stretches (CH), CCH bends (CCH) and CCC bends (CCC); the hydroxyl CO stretch (CO P), OH stretch (OH P), CCO bend (CCOP) and COH bend (COHP); the formyl CC stretch (CC B), CH stretch (CH B), CO stretch (CO B), CCC bend (CCCB), OCH bend (OCHB) and CCO bend (CCOB); and the methoxyl CO stretch (CO), OC stretch (OC), CH stretches (CH), CCO bends (CCOM), COC bend (COCM), OCH bends (OCH) and HCH bends (HCH).

The assignments proposed in this investigation are presented in Table XLVII. The assignments of the substituent sensitive phenyl modes and the substituent modes are discussed in this section.

TABLE XLVI

CONDENSED POTENTIAL ENERGY DISTRIBUTION FOR THE A" VIBRATIONS OF VANILLIN

Wavenumber, cm^{-1}		Error		Potential Energy Distribution
Observed	Calculated	cm^{-1}	%	Internal Coordinate,[a] %
2969	2951	18	0.62	CHM(99)
1437	1441	-4	-0.29	HCHM(78) OCHM(22)
1165	1155	10	0.86	OCHM(77) HCHM(21)
1005	1004	1	0.05	WAGO(64) WAG(18) WAGH(10)
937	954	-17	-1.79	WAG(86) TOR(23) WAGO(10)
874	888	-14	-1.55	WAG(91) TOR(20)
812	837	-25	-3.07	WAG(83) TOR(14)
732	734	-2	-0.33	WAGM(36) WAGP(36) TOR(16)
555	571	-16	-2.81	WAGC(34) TOR(25) WAGM(10)
452	453	-1	-0.19	WAGP(31) WAGM(29) TOR(19)
378	385	-7	-1.91	TORP(26) TOR(18) WAGC(16)
345	307	38	10.89	TORP(71) TOR(11)
265	270	-5	-1.90	TORM(62) TOR(22)
195	200	-5	-2.54	TORM(32) TOR(25)
172	184	-12	-7.06	TORB(44) TOR(31)
122	125	-3	-2.39	TORO(61) TORB(24)
85	85	0	-0.52	TORO(41) TOR(35) TORB(21)
Average Error		10	2.28	

[a]The internal coordinates are the phenyl wags (WAG) and torsions (TOR); the hydroxyl wag (WAGP) and torsion (TORP); the formyl wag (WAGC), CH wag (WAGH), CO wag (WAGO) and torsion (TORB); and the methoxyl wag (WAGM), CH stretch (CHM), HCH bend (HCHM), OCH bend (OCHM), C-OCH_3 torsion (TORO) and CO-CH_3 torsion (TORM).

Phenyl Modes

Nine of the thirty fundamental phenyl modes of vanillin are associated with the CX bonds, i.e., there is a CX stretch, an in-plane and an out-of-plane CCX bend associated with each of the three CX bonds. These modes are substituent sensitive. Additionally, the in-plane and out-of-plane ring deformations, modes 1, 12, 6a, 6b, 4, 16a and 16b appear to be substituent sensitive. The potential

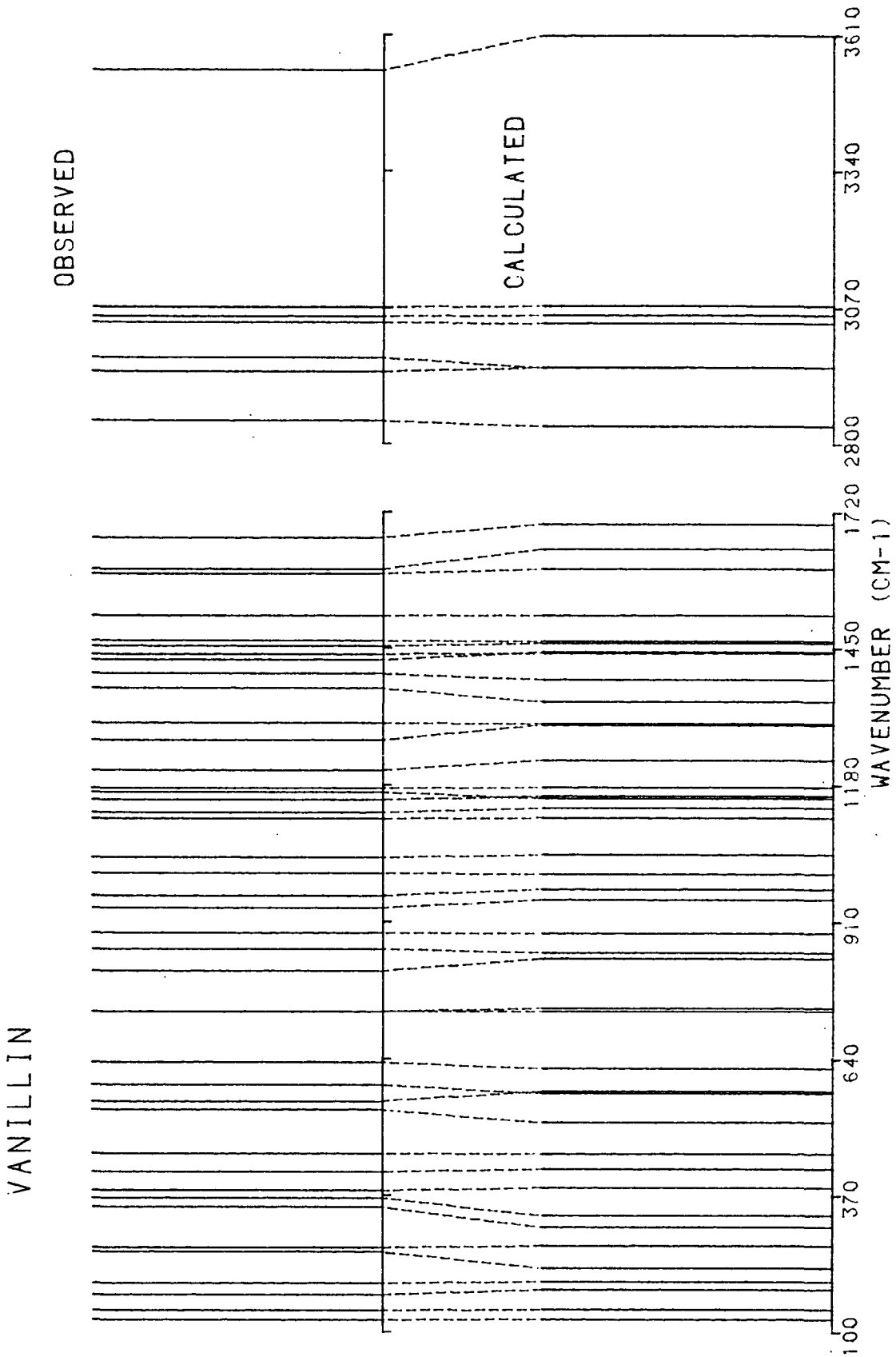


Figure 29. Comparison of the calculated and the observed spectra of vanillin.

TABLE XLVII

ASSIGNMENT OF THE NORMAL MODES OF VANILLIN

Infrared, cm^{-1}	Raman, cm^{-1}	Assignment
	(85)	16b A" ring deformation
	122 s[a]	A" C-OCH torsion
	141 s	9b A' CCX bend
	172 w	A" CHO torsion
	195 s	16a A" ring deformation
	257 w	15 A' CCX bend
	265 w	A" O-CH torsion
	345 w	A" OH torsion
	363 w	18b A' CCX bend
	378 w	4 A" ring deformation
	429 m	6a A' ring deformation
450 w	452 w	11 A" CCX bend
537 m	538 m	6b A' ring deformation
556 w	555 w	10b A" CCX bend
588 m	588 w	A' HCO bend
635 s	632 w	A' COC bend
666 w		10a A" CCX bend
734 s	732 m	1 A' ring deformation
815 m	812 m	17b A" CCH bend
855 m	857 w	12 A' ring deformation
875 m	874 w	17a A" CCH bend
937 w	937 w	5 A" CCH bend
960 m	960 w	18a A' CCH bend
	1005 w	A" H-CO wag
1030 s	1029 m	A' O-CH stretch
1113 m	1114 w	A' methyl rock
1123 s	1124 m	9a A' CCH bend
1150 vs	1154 s	7b A' CX stretch
1165 sh		A" methyl rock
1173 s	1172 s	A' COH bend
1208 s	1206 m	13 A' CX stretch
1269 vs	1267 s	7a A' CX stretch
1301 s	1301 w	14 A' CC stretch
1378 m	1371 m	3 A' CCH bend
1399 m	1401 m	A' HC=O bend
1428 s	1426 m	A' sym HCH bend
1437 s	1434 m	A" asym HCH bend
1451 m	1453 s	19b A' CC stretch
1466 s	1464 m	A' asym HCH bend
1515 vs	1515 m	19a A' CC stretch
1596 s	1593 s	8a A' CC stretch
1605 s	1603 s	8b A' CC stretch
1698 s	1697 vs	A' C=O stretch
2732 w	2733 w	A' H-CO stretch
2845 m	2843 w	A' sym CH stretch
2940 m	2942 w	A' asym CH stretch
2972 w	2969 w	A" asym CH stretch
3040 w	3040 w	A' CH stretch
	3052 m	A' CH stretch
3070 w	3070 m	A' CH stretch
3538 m	3535 w	A' OH stretch
	3611 vw	

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

energy distribution shows the vibrations associated with the CX bonds to be highly coupled. As in the disubstituted benzenes, the frequencies are attributed to the coordinate making the major contribution to the band.

The CX stretching mode, the in-plane bend and the out-of-plane bend of the C-OH group are assigned to bands at 1208, 363, and 452 cm^{-1} in the spectra of vanillin. For comparison, these modes were assigned to bands at 1223, 346, and 456 cm^{-1} in guaiacol. The three modes associated with the C-OCH_3 band are assigned at 1267, 141, and 732 cm^{-1} in vanillin, corresponding to the bands at 1263, 236 and 741 cm^{-1} in guaiacol. And the three modes associated with the C-CHO bond of vanillin are assigned at 1150, 363, and 555 cm^{-1}. In m-anisaldehyde these bands were assigned at 1192, 458, and 518 cm^{-1}.

The in-plane ring deformations in trisubstituted benzenes were classified by Varsanyi (6) as x-sensitive modes. These modes (1, 12, 6a and 6b) are identified as x-sensitive in this investigation and are assigned at 732, 855, 416 and 538 cm^{-1}. The out-of-plane ring deformations, modes 4, 16a and 16b, are also classified as x-sensitive modes in this investigation. They were not so labeled by Varsanyi. The first two of these modes are assigned at 378 and 195 cm^{-1}, the last, calculated to arise at 85 cm^{-1} but unobserved, is not assigned.

Substituent Modes

Twenty-one of the fifty-one fundamental modes of vanillin can be attributed to the vibrations of the substituent groups. Three of these are hydroxyl modes, six are formyl modes and twelve are vibrations of the methoxyl group. The hydroxyl, the formyl and ten of the methoxyl groups have previously been assigned. The substituent modes are assigned in this investigation using the results of the normal coordinate calculations supplemented with group frequency information and spectral data.

Tariq (121) assigned the OH stretch, the in-plane OH bend and torsion of the hydroxyl group to bands at 3540, 1200 and 710 cm^{-1} (for solid vanillin). Puttnam (104) assigned the OH stretch at 3542 cm^{-1}.

In this investigation the OH stretch, COH in-plane bend and out-of-plane bend of the hydroxyl group are assigned at 3538, 1173 and 345 cm^{-1}. These modes were assigned to bands at 3610, 1180 and 309 cm^{-1} in the spectra of phenol. These assignments agree with those proposed by Puttnam (104) and Tariq (121).

Tariq (121) also assigned the six formyl modes. He assigned the CH and C=O stretches at 2860 and 1670 cm^{-1}, the in-plane CCH and CC=O bends at 1400 and 810 cm^{-1}, the out-of-plane wag of the formyl hydrogen at 175 cm^{-1} and the CHO torsion at 125 cm^{-1}. Saier, et al. (44) found two bands in the region characteristic of aldehyde CH stretching modes, at 2812 and 2717 cm^{-1}. The band at the lower wavenumber was assigned as the fundamental.

The six modes of the formyl group, the CH and C=O stretches, the in-plane COH and CCO bends, the out-of-plane CH wag and the C-CHO torsion are assigned at 2722, 1669, 1399, 588, 1005, and 172 cm^{-1} in this study. In benzaldehyde these modes were assigned to bands observed at 2737, 1700, 1394, 649, 1008 and 128 cm^{-1}. This assignment of the CH stretch agrees with Saier's assignment (44). As in benzaldehyde, 4-hydroxybenzaldehyde and m-anisaldehyde, two absorption bands are observed between 2600 and 2900 cm^{-1} where the aldehydic CH stretch should occur, at 2737 and 2820 cm^{-1}. These are interpreted as resulting from a Fermi resonance interaction between the CH stretching fundamental and the first overtone of the aldehydic CH bending vibration (44). The fundamental is assigned at 2737 cm^{-1}. Tariq's assignments of the CH stretch, the in-plane C=O bend, the out-of-plane CH wag and the torsion differ from the assignments proposed in this investigation.

Tariq assigned the three CH stretching modes of the methoxyl group at 2980, 2940, and 2840 cm^{-1}. Two of the three methoxyl HCH bends and one of the two OCH bends he assigned to bands at 1450, 1380, and 1175 cm^{-1}. And the O-CH_3 stretch, the COC bend, the O-CH_3 torsion and the C-OCH_3 torsion were assigned at 1030, 350, 200, and 100 cm^{-1} (121).

Briggs, et al. (53) list eight bands they associate with the methoxyl group of vanillin in their study of methylenedioxy and aryl ether groups. Five of these bands are assigned. Bands at 2967 and 2849 cm^{-1} are attributed to two of the CH stretching modes. The band at 1464 cm^{-1} was assigned as an antisymmetric HCH bend. The 1271 and 1032 cm^{-1} bands were attributed to the C-OCH_3 and O-CH_3 stretching modes, respectively. Bands at 3012, 2924, and 1127 cm^{-1} were also cited as characteristic of a methoxyl group but were not assigned.

Seven of the twelve methoxyl modes belong to the A' symmetry species: a symmetric and an antisymmetric CH stretch, a symmetric and an antisymmetric HCH bend, an OCH bend, a COC bend and the O-CH_3 stretch. In this investigation, these are assigned to bands at 2844, 2942, 1426, 1464, 1124, 632, and 1036 cm^{-1} in the vibrational spectra of vanillin, and at 2833, 2945, 1441, 1468, 1112, 553, and 1040 cm^{-1} for anisole. The remaining five methoxyl modes are A" modes: an antisymmetric CH stretch, HCH bend and OCH bend, and the two torsions about the C-OCH_3 and O-CH_3 bonds. These are assigned to peaks at 2969, 1437, 1165, 265 and 122, cm^{-1} in this study. In anisole these modes were assigned at 2957, 1456, 1154, 285, and 115 cm^{-1}. These assignments agree with those proposed by Briggs (53) but differ from Tariq's (121).

Comparison of the Normal Modes of Vanillin

To ascertain the effect of trisubstitution on the frequencies and intensities of the normal modes of the aromatic ring, the assignments of these bands

in vanillin are compared to the assignments of these bands in the mono- and disubstituted compounds. The behavior of the substituent bands on further substitution of the ring is also noted.

Frequency

Based on their frequencies, substituent sensitive and substituent insensitive phenyl modes are identified. The frequencies of the substituent modes appear to be little influenced by other substituents.

Sixteen of the normal modes of the aromatic ring are classified as x-sensitive in this investigation. The x-sensitive modes comprise the four in-plane ring deformations, modes 1, 12, 6a and 6b, the three out-of-plane ring deformations, modes 4, 16a and 16b, and the nine modes associated with the three CX bonds. The four in-plane ring deformations, two of the out-of-plane ring deformations (16a and 16b) and six modes associated with the CX bonds are considered to be x-sensitive in disubstituted benzenes. The x-insensitive bands are due to the CH stretching modes (2, 20a and 20b), the CC stretching modes (8a, 8b, 14, 19a and 19b), the CH in-plane bending modes (3, 15 and 18b) and the out-of-plane CH wags (5, 17a and 17b). The frequencies of these modes are shifted slightly from those of benzene, but not to the extent of the x-sensitive bands. The frequencies of the phenyl modes of vanillin and the disubstituted benzenes are shown in Table XLVIII.

The wavenumbers of the substituent modes in the mono-, di- and trisubstituted benzenes are listed in Table XLIX. These modes are virtually unaffected by increasing the extent of substitution of the ring.

Intensities

The intensities of the phenyl bands are affected by substitution of the ring. Comparison of the intensities of the phenyl bands of vanillin to the

intensities of these bands of the mono- and disubstituted benzenes reveals few regularities. The intensities of the substituent bands, like their frequencies, are less influenced by other substituents on the ring.

TABLE XLVIII

WAVENUMBERS (CM^{-1}) OF THE BENZENE MODES AND THE PHENYL MODES OF MONO-, DI- AND TRISUBSTITUTED BENZENES

Mode	Benzene	Phenol	Benz-aldehyde	Anisole	4-Hydroxy-benz-aldehyde	Guaiacol	m-Anis-aldehyde	Vanillin
				In-plane Modes				
2	3064	3087	3088	3093	3086	3091	3071	3070
7b	3055	3076	3065	3069	3063	3070	3060	1150
20a	3055	3061	3045	3055	3042	3054	3056	3052
20b	3043	3046	3035	3037	3022	3023	3035	3040
8b	1594	1605	1600	1600	1598	1615	1599	1605
8a	1594	1595	1588	1587	1588	1596	1589	1596
19a	1483	1499	1496	1497	1519	1502	1486	1515
19b	1483	1471	1458	1455	1450	1470	1466	1453
3	1348	1388	1314	1336	1315	1357	1324	1371
14	1309	1345	1288	1304	1286	1301	1286	1301
13	3037	1251	1205	1248	1240	1263	1266	1267
7a	3043	3022	3026	3033	1218	1223	1192	1208
15	1149	1152	1162	1172	451	534	458	257
9a	1179	1168	1168	1181	1140	1172	1149	1124
18b	1039	1071	1072	1078	1112	1134	1079	363
18a	1039	1024	1023	1021	1015	1027	983	960
12	1012	1000	1002	995	789	834	994	855
1	999	812	830	784	861	786	745	732
6b	608	618	615	615	645	583	647	538
6a	608	530	439	443	402	502	470	429
9b	1179	416	226	266	222	236	167	141
				Out-of-Plane Modes				
5	990	986	989	975	964	962	952	937
17a	968	958	962	960	947	917	901	874
17b	968	890	924	885	835	852	868	812
10a	850	818	851	820	825	759	788	732
10b	850	509	451	513	507	456	447	555
4	704	690	689	692	667	570	684	452
11	672	756	746	757	349	741	518	378
16a	404	416	410	415	415	310	230	195
16b	404	242	237	214	179	188	209	85

TABLE XLIX

WAVENUMBERS (CM^{-1}) OF THE SUBSTITUENT MODES OF DI- AND TRISUBSTITUTED BENZENES

Mode	Phenol	Benz-aldehyde	Anisole	4-Hydroxy-benz-aldehyde	Guaiacol	m-Anis-aldehyde	Vanillin
			A' Modes				
OH stretch	3602			(3300)	3556		3538
CH stretch			2945		2950	2942	2942
CH stretch			2833		2840	2844	2844
CH stretch		2737		2754		2731	2722
C=O stretch		1700		1679		1669	1698
HCH bend			1468		1461	1460	1464
HCH bend			1441		1454	1435	1426
O=CH bend		1394		1387		1385	1399
COH bend	118 .0			1162	1208		1173
OCH bend			1112		1040	1087	1112
O-CH stretch			1040		1109	1040	1030
HCC bend		649		604		230	588
COC bend			553		346	554	632
			A" Modes				
CH stretch			2957		2965	2964	2969
HCH bend			1456		1443	1436	1437
OCH bend			1154		1155	1164	1165
CH wag		1008		1010		1005	1005
OH torsion	309			337	346		345
O-CH torsion			(285)		236	279	265
CHO torsion		128		106		134	172
C-OCH torsion			(115)		108	(97)	122

The nature of the substituents, the pattern of substitution, and the form of the mode all influence the intensity of the IR and Raman bands. For this reason, few regularities are expected, or found, in the intensities of the phenyl modes of the mono-, di- and trisubstituted benzenes. The patterns that are present are due to the particular substituents and arrangement of these substituents in the compounds studied and do not necessarily extend to benzenes with different substituents. For example, normal mode 8 involves the movement of the opposite sides of the ring toward and away from each other. In benzene and in

p-di-x-substituted benzenes there will be no change in the overall dipole moment during the vibration. The band will not appear in the IR. However, if the nature of the p-substituents differ considerably (e.g., monosubstitution of a strong electron donor or acceptor or p-disubstitution of an electron donor and an electron acceptor) there would be a significant change in the overall dipole moment, giving rise to a strong IR band. Since the hydroxyl and methoxyl groups are strong electron donors and the formyl group is a strong electron acceptor, these bands are strong in the spectra of all seven model compounds regardless of the pattern of substitution. Also, due to the natures of the substituents the CX stretching modes all have strong IR bands and medium to strong Raman bands. As in the mono- and disubstituted compounds, the intensities of the IR and Raman bands can be rationalized to some extent if the nature of the substituents and the forms of the modes are known.

The potential energy distributions of the vanillin bands show many of the substituent modes to be rather pure substituent bands, with little coupling with the phenyl ring or other substituent modes. The intensities of these bands are the same in vanillin as in the mono- and disubstituted benzenes. The intensities of the bands of substituent modes that are coupled with other vibrations vary somewhat in intensity depending on the extent of coupling (i.e., the form of the mode).

SUMMARY

The IR and Raman spectra of the trisubstituted benzene, vanillin, were assigned using normal coordinate calculations, group frequency information and spectral data. The normal coordinate calculations were based on a modified valence force field using force constants transferred from the MVFF's developed

for the monosubstituted benzenes. The assignments of these spectra were compared with the assignments of the mono- and disubstituted benzenes to determine the effect of trisubstitution on the phenyl modes, and of further substitution on the substituent modes.

Based on frequency shifts, sixteen of the normal modes of the phenyl group are identified to be substituent sensitive. These sixteen modes comprise the nine vibrations associated with the three CX bonds and the seven in-plane and out-of-plane ring deformations. The remaining fourteen phenyl modes are classified as substituent insensitive. The frequencies of the substituent modes are little influenced by the other substituents on the ring. The intensities of the phenyl bands vary between the mono-, di- and trisubstituted benzenes studied. Of these bands only the in-plane CC stretching modes, vibrations 8a and 8b, are consistently strong bands. The intensities of the substituent bands are less variable, most having the same intensity in vanillin as in the monosubstituted compounds.

CHAPTER V. LIGNIN

INTRODUCTION

The objective of this thesis is to investigate the vibrational spectra of lignin model compounds. The interpretation of the vibrational spectra of such compounds should help in understanding the vibrational spectra of lignins. This chapter explores how the results of this investigation can be applied to the interpretation of the vibrational spectra of lignins.

LITERATURE REVIEW

The infrared spectra of isolated lignins have been extensively studied. These spectra have been interpreted based on group frequency analysis. Few Raman spectra of lignins have been reported.

INFRARED SPECTRA

The first formal investigation of the vibrational spectra of lignin was by E. J. Jones in 1949 (122). At that time little was known about lignin. Jones' investigation was undertaken with the hope that the development of a new tool would "be capable of speeding up the elucidation of the composition of lignin". Working with Brauns' native spruce lignin, Jones tentatively assigned several of the bands in the IR spectra of lignins.

Since 1949 the infrared spectra of isolated lignins have been extensively studied. Hergert reviewed what was known about the infrared spectra of lignins in 1971 in Sarkanen's book, Lignins (123). Little has been done in recent years to further the understanding of the infrared spectra of lignin; most studies of the IR spectra of lignin involve application of the existing interpretation of the IR spectra to some facet of lignin chemistry.

Infrared spectroscopy has been used to compare lignins isolated by differing isolation procedures or isolated from different sources (123). These prepared lignins are either insoluble in organic solvents, or only soluble in polar solvents which form hydrogen bonds with lignin. IR spectra are therefore measured on finely ground solid samples as KBr disks or paraffin mulls, or as thin films obtained by evaporation of a solution on a salt plate. IR difference spectra have also been reported for lignins. These spectra were measured with finely ground samples of wood or thin wood sections in the sample beam and delignified samples in the reference beam, or by subtracting the spectrum of a delignified sample from that of a whole wood spectrum (123). The orientation of the wood sections with respect to any polarization of the incident light was not taken into consideration.

RAMAN SPECTRA

Little has been published on the Raman spectra of lignins. Schulz published the Raman spectra of alkaline solutions of Bjorkman spruce and beech lignins in 1980 (124). These spectra have many relatively intense bands in the 1800-2500 cm^{-1} region which should not be present in Raman spectra of such solutions. Atalla recorded a Raman difference spectrum of Loblolly pine lignin in 1979. Assignments for these spectra have not been discussed. Since Raman spectra provide information complementary to infrared absorption measurements, an understanding of the Raman spectra of lignins should significantly add to the understanding of the structure of lignin.

DISCUSSION OF LIGNIN ASSIGNMENTS

In the past, the IR spectra of lignins have been interpreted by group frequency analysis, comparison to the spectra of lignin model compounds and

comparison to the spectra of lignin derivatives. Normal coordinate analysis has not been used to interpret these spectra due to "the amorphous nature of lignin, the complexity of individual monomeric units, and the random order in which they are linked" (123). Band assignment was somewhat empirical, but due to the variety of methods used to make the assignments Hergert considered the majority of the assignments he included in his review (123) to be accurate.

Wood lignins have been classified into two major categories, hardwood and softwood lignins. The latter is comprised primarily of guaiacyl units, whereas the former has an equal proportion of guaiacyl and syringyl units. Correspondingly, two major categories of lignin IR spectra have been identified, hardwood and softwood. Within each of these classes though, it was found that the differences in the spectra of various lignin preparations were more sensitive to the type of isolation procedure used than to a variation in species. Observations of this nature provide additional incentive for developing a means of investigating the structure of lignin in situ.

The results of this investigation of the vibrational spectra of lignin model compounds can be used to further the interpretation of the vibrational spectra of lignin. The three substituents present are representative of the types of substituents found in softwood lignins. So, the fourteen phenyl bands identified to be substituent insensitive on trisubstitution of the benzene ring are likely to occur at the same frequencies in softwood lignins as in vanillin. The substituent bands insensitive to other substituents on the ring would also be expected to arise at the same frequencies in softwood lignins as in vanillin.

The assignments of the IR spectra of lignins as reviewed by Hergert, and the lignin assignments that can be made based on the interpretation of the

spectra of the model compounds are compared in this section. A couple of the more recent IR assignments are also discussed. Both past lignin assignments and the assignments proposed for vanillin are listed in Table L.

TABLE L

PROPOSED ASSIGNMENTS FOR THE VIBRATIONAL SPECTRA OF LIGNINS

Softwood, cm^{-1}	Lignin Assignments[a]	Vanillin, cm^{-1}	Vanillin Assignments
3425-3400	OH stretching (H-bonded)	3535	OH stretch
		3070	CH stretch, phenyl
		3052	CH stretch, phenyl
		3040	CH stretch, phenyl
2920	CH stretch in methyl and methylene groups	2969	CH stretch, methoxyl
		2942	CH stretch, methoxyl
2875-2850	"	2843	CH stretch, methoxyl
2820	"	2733	CH stretch, formyl
1715	Carbonyl stretch, unconj.	1697	C=O stretch
1675-1660	Carbonyl stretch, para substituted aryl ketone		
1605	Aromatic skeletal vib.	1603	CC stretch, phenyl
		1593	CC stretch, phenyl
1515-1510	"	1515	CC stretch, phenyl
1470	CH deformations, asym.	1464	HCH bend, methoxyl
1460	"	1453	CC stretch, phenyl
1430	Aromatic skeletal vib.	1434	HCH bend, methoxyl
		1426	HCH bend, methoxyl
		1401	HC=O bend
1370	CH deformation, sym.	1371	CCH bend
1270	Ring breathing with	1267	CX stretch, methoxyl
1270	HCH asym vibrations (125)		
1270	methylene vibrations (127)		
1230	"	1206	CX stretch, hydroxyl
		1172	COH bend
		1165	OCH bend, methoxyl
1140	Aromatic CCH bend	1154	CX stretch, formyl
		1124	CCH bend
		1114	OCH bend, methoxyl
1035	Aromatic CCH bend	1029	O-CH_3 stretch
1035	COC vibrations (773)		
		1005	H-CO wag, formyl
970	=CH out-of-plane bend	960	CCH bend
		937	CCH wag
		874	CCH wag
855	Aromatic CH wag	857	Ring deformation
815	"	812	CCH wag
750-770	"	732	Ring deformation

[a]Lignin assignments are from Hergert's review (123) unless otherwise specified.

PHENYL MODES

Hergert (123) found that three absorption bands in lignin spectra were identified as aromatic skeletal vibrational modes: 1595-1605, 1505-1515, and 1420-1450 cm^{-1}. The band at ca. 1600 cm^{-1} was assigned as a relatively pure ring stretching frequency that may be strongly associated with the stretching mode of a ring C-O bond. Model compound studies showed an increase in the intensity of this band as the number of CO bonds is increased. The intensity of this band was noted to increase even more on conjugation with an α-carbonyl group. The other two bands, at 1510 and 1435 cm^{-1} were proposed to be ring-stretching modes strongly coupled with CH in-plane deformations. The intensity of the 1435 cm^{-1} band was found to be sensitive to the nature of the ring substituents. The intensity of the 1510 cm^{-1} vibration was fairly constant. The relative intensities of the 1600 and 1510 cm^{-1} bands are used to differentiate between hardwood and softwood lignins. In softwood lignins the intensity of the 1600 cm^{-1} band is noticeably lower than that of the 1510 cm^{-1} band. The presence of the syringyl units in hardwood lignins increases the intensity of 1600 cm^{-1} band, so the intensities of the two bands are approximately equal. Similar behavior is observed with the 1510 and 1435 cm^{-1} bands.

The bands at 1270, 1230 and 1130 cm^{-1} in guaiacyl compounds, and at 1335 and 1235 cm^{-1} in syringyl derivatives were previously assigned to ring breathing modes coupled with C-O stretching (123). Softwood bands at 1160 and 1040 cm^{-1} and the hardwood band at 1130 cm^{-1} were assigned to aromatic CH in-plane deformation modes. The relative intensities of these bands were thought to give an indication of the methoxyl content of the lignin (123).

Gol'man attributed the bands at 1035 cm^{-1} in softwoods and at 1030 cm^{-1} in hardwoods to the symmetric valence vibrations of the COC bonds of the methoxyl

groups on the aromatic ring. He ascribed bands at 1270 cm^{-1} in softwoods and at 1275 cm^{-1} in hardwoods to the asymmetric vibrations of the methoxyl HCH bonds. These assignments were based on the study of a large number of lignin model compounds (125,126).

In a refinement of his earlier interpretation of the lignin spectrum, Pilipchuk asserted that the band at 1270 cm^{-1} should be attributed to methylene groups rather than to the deformational vibrations of the methoxyl groups. He also attributed the band at 1330 cm^{-1} to the deformational vibrations of the methoxyl groups in syringyl units (127).

The aromatic CH out-of-plane vibrations are known to appear in the 750-900 cm^{-1} region. The 850-880 cm^{-1} and 800-855 cm^{-1} bands in guaiacyl compounds were respectively assigned to the isolated hydrogen and to the two adjacent ring hydrogen deformations. In syringyl compounds there is only one type of ring hydrogen. The out-of-plane deformation of this bond was assigned at 830-860 cm^{-1}. The far infrared region (650-50 cm^{-1}) has not been as extensively investigated. Skeletal bending modes make the largest contributions in this region. It was observed that softwood lignins generally have bands at 560 and 470 cm^{-1}, and that hardwood lignins absorb at 535 cm^{-1} (123).

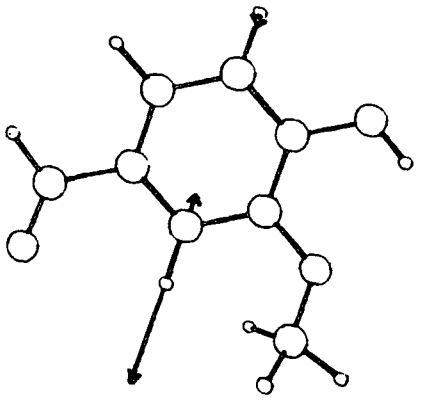
Three CH stretching modes, five CC stretching modes, three in-plane CH bending modes, and three out-of-plane CH wags are identified as the x-insensitive modes of vanillin in this investigation. The CH stretching modes of lignin would be expected to arise between 3020 and 3080 cm^{-1}. The CC stretching modes 8a and 8b should occur at 1600 ± 15 cm^{-1}, modes 19a and 19b should arise in the range 1483 ± 30 cm^{-1} and vibration 14 should occur at ca. 1300 cm^{-1}. The CH in-plane bending modes, 9a, 18a and 3 occur at 1112, 960, and 1371 cm^{-1} in vanillin.

The out-of-plane wags, modes 5, 17a and 17b are assigned at 937, 887, and 812 cm^{-1}. Of these subtituent insensitive modes, the CH and CC stretching modes are the most constant in frequency.

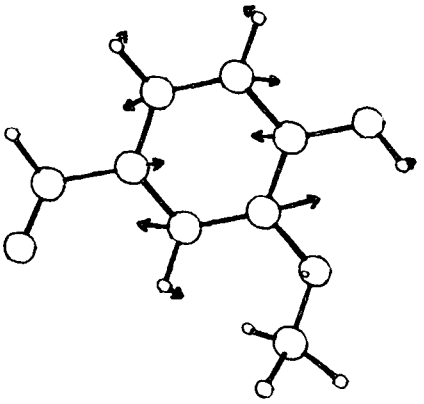
Though constant in frequency, the intensities of these bands are sensitive to the substituents. The substituents present in vanillin are thought to be common in softwood lignins. Therefore the intensities of these bands can be predicted based on their intensities in vanillin. The CH stretching bands are weak in both the IR and Raman effects. The CC stretching modes vary in intensity. Modes 8a and 8b are strong in both the IR and Raman spectra, with the higher frequency band more intense in the IR, and the lower frequency band more intense in the Raman. The band due to mode 19a is very strong in the IR and of medium intensity in the Raman. The reverse is true of mode 19b, it has a strong band in the Raman effect and a medium band in the IR. Mode 14 is credited with a strong IR band, but a weak Raman band. The three in-plane CH bending modes give rise to IR bands of medium intensity and medium or weak Raman bands. The out-of-plane CH wags have medium-weak IR and Raman bands. The forms of these substituent insensitive modes in vanillin are shown in Fig. 30.

The assignments proposed for the vibrational spectra of vanillin do not support several of the assignments suggested in Hergert's review (123). Bands at 1270, 1230, and 1130 cm^{-1} in guaiacyl and at 1335 and 1235 cm^{-1} in syringyl derivatives were identified in Hergert's review to be ring breathing modes coupled with CO stretching. Based on the proposed assignments for vanillin, this interpretation is not strictly correct. The two breathing modes of the aromatic ring, modes 1 and 12, arise at 732 and 855 cm^{-1} in vanillin. Based on their potential energy distributions (Table XLV), these modes do appear to be

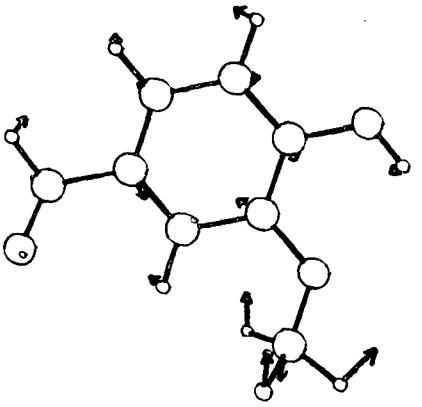
Normal Mode 20A = 3052 cm^{-1}



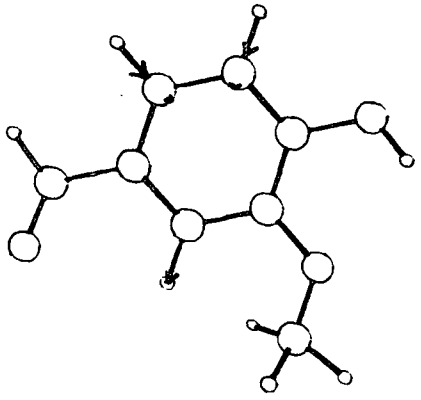
Normal Mode 8B = 1605 cm^{-1}



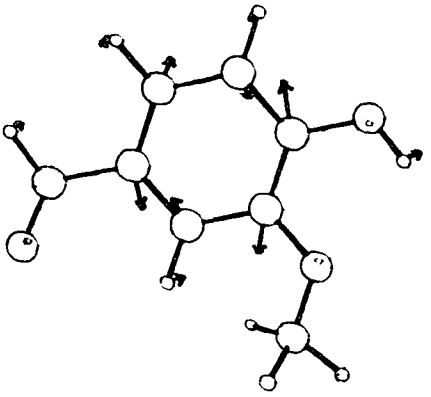
Normal Mode 19B = 1453 cm^{-1}



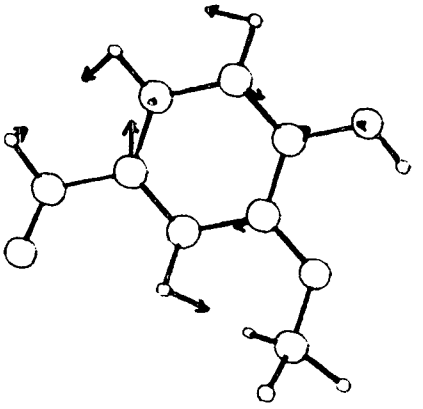
Normal Mode 2 = 3070 cm^{-1}



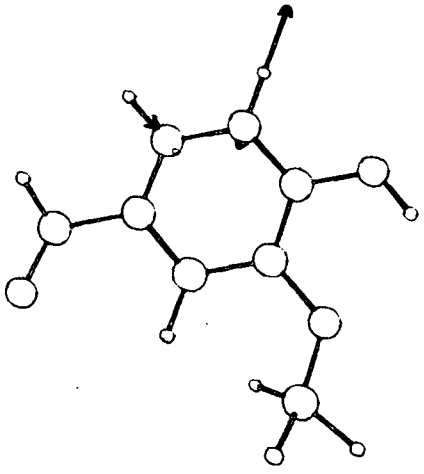
Normal Mode 8A = 1596 cm^{-1}



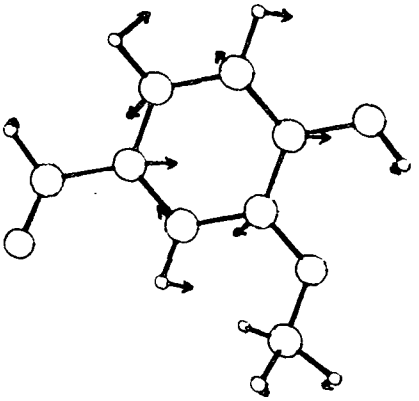
Normal Mode 14 = 1301 cm^{-1}



Normal Mode 20B = 3040 cm^{-1}



Normal Mode 19A = 1515 cm^{-1}



Normal Mode 3 = 1371 cm^{-1}

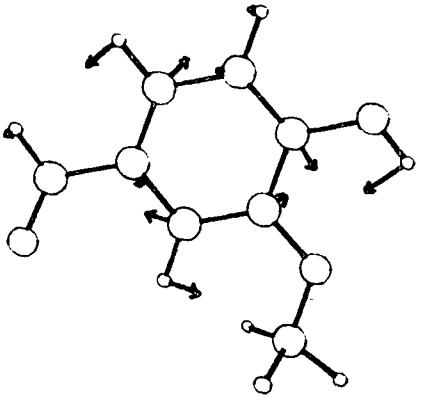
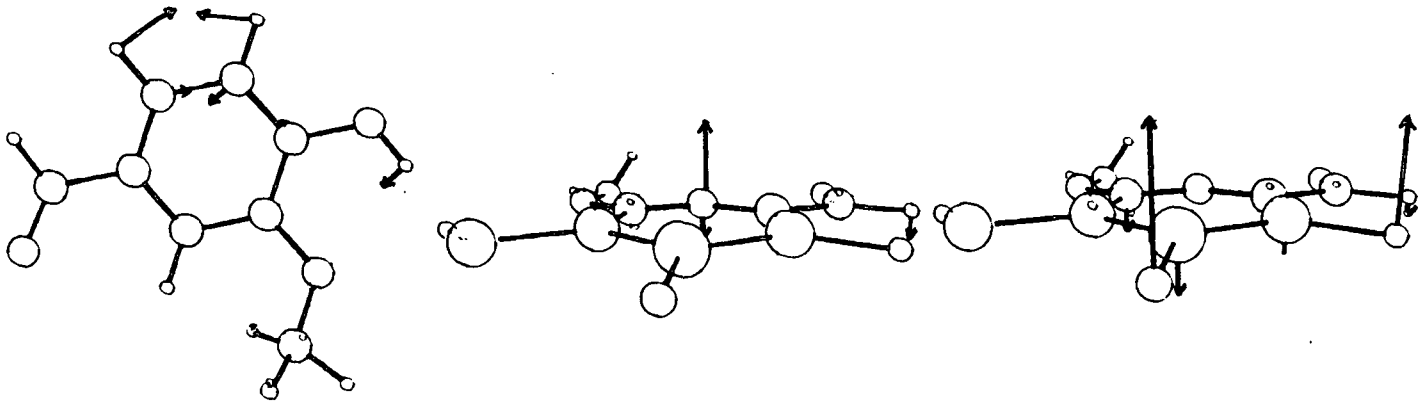


Figure 30. The substituent insensitive phenyl modes of vanillin.

Normal Mode 9A = 1124 cm^{-1} Normal Mode 17A = 874 cm^{-1} Normal Mode 17B = 812 cm^{-1}



Normal Mode 18A = 960 cm^{-1} Normal Mode 5 = 937 cm^{-1}

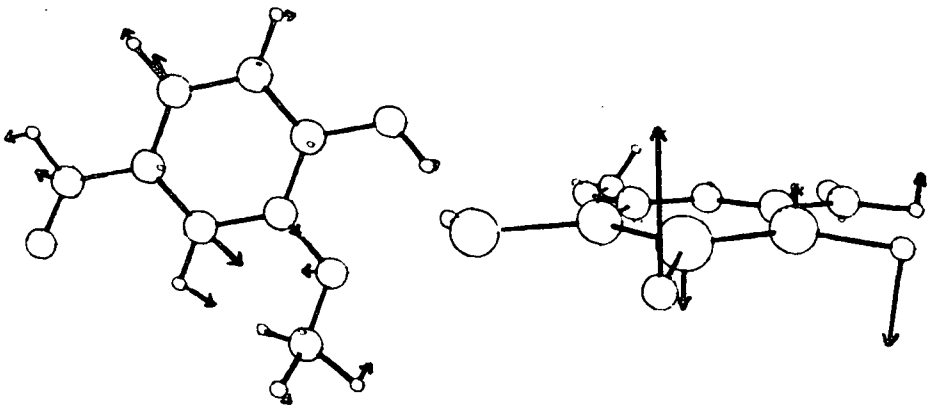


Figure 30 (Continued). The substituent insensitive phenyl modes of vanillin.

coupled with CO stretching modes. However, the frequencies of these ring breathing modes are not expected to be shifted significantly in the vibrational spectra of lignins. Any increase in the mass of the substituents is expected to lower the frequencies of these modes (6). So bands arising at 730 and 850 cm^{-1}, not at 1270 and 1230 cm^{-1}, would be expected to be ring breathing modes coupled with CO stretching modes. The C-O stretching modes of the methoxyl and hydroxyl

groups are assigned at 1267 and 1208 cm^{-1}. These modes are derived from the CH stretching modes of benzene and involve motion of other substituent groups and the ring. This suggests assignment of the guaiacyl bands at 1270 and 1230 cm^{-1} to CO stretching modes coupled with other substituent vibrations. Vanillin has a CCH bending mode at 1124 cm^{-1}. This supports the assignment of a hardwood band at 1130 cm^{-1} to aromatic CH in-plane deformation, not the softwood assignment to a CO stretch coupled with ring breathing. Guaiacyl bands at 1160 and 1040 cm^{-1} were identified in Hergert's review as aromatic CH in-plane bending modes. Bands occurring at these frequencies in vanillin are attributed to vibrations of the methoxyl group.

The assignments suggested by Gol'man (125,126) are not supported by the vanillin assignments either. The band at 1036 cm^{-1} in vanillin is assigned as a $O-CH_3$ stretch rather than as the COC bend as proposed by Gol'man. The band at 1267 cm^{-1} is attributed to the $C-OCH_3$ stretch in vanillin, not to deformations of the methoxyl HCH bonds.

The proposed assignments for vanillin parallel the rest of the lignin assignments reported in the literature. Hergert classified three absorption bands in lignin spectra as aromatic skeletal vibrational modes: 1595-1605, 1505-1515 and 1420-1450 cm^{-1}. Bands arising in these ranges have been classified as aromatic CC stretching modes in the vanillin spectrum. The aromatic CH out-of-plane vibrations were identified in the 750-900 cm^{-1} region in Hergert's review. The 850-880 cm^{-1} and 800-855 cm^{-1} bands in guaiacyl derivatives were assigned to the isolated hydrogen and to the two adjacent ring hydrogen deformations, respectively. Bands occurring in these regions were similarly assigned in the spectra of vanillin.

SUBSTITUENT MODES

The hydroxyl groups in lignins were noted to be responsible for bands in two different regions of the infrared spectra of lignins: the OH stretching bands arise in the 3000-3700 cm^{-1} region and the C-O stretch and C-O and O-H bends are found in the 900-1200 cm^{-1} range (123). The OH stretching bands of aliphatic hydroxyl groups occur at somewhat higher frequencies than those of phenolic hydroxyl groups.

Hergert (123) found that the bands at 2800-2940, 1460-1470, and 1365-1370 cm^{-1} were ascribed to aliphatic CH stretches and bends. However, it was noted that whether the bands originate from C-methyl, methoxyl or methylene CH bonds is not easily determined. In a study of lignin model compounds, Sarkanen found that there was no simple relationship between the number of methyl groups and the intensity of the absorption bands at 1460-1470 cm^{-1}, which have been assigned to the asymmetric bending of methyl groups (128).

The carbonyl group is probably the most studied functional group in IR spectra, and lignin spectra are no exception. Different types of carbonyl groups have characteristic frequencies within the 1600-1750 cm^{-1} range (123). This region is relatively free of other absorption bands. Given the spectra of appropriate lignin derivatives the type of carbonyl group present should be discernible.

In this investigation, the frequencies and intensities of most of the substituent modes of vanillin were noted to be insensitive to other substituents on the ring. They would therefore be expected to arise at approximately the same frequencies in the spectra of lignins. The stronger bands would probably be the easiest to identify in the vibrational spectra of lignins.

The characteristic vibrations of the hydroxyl groups are the OH stretch, the in-plane COH bend and the OH torsion. For free OH groups these modes are assigned at 3538, 1173, and 345 cm^{-1} in vanillin. The OH stretch and torsion give rise to weak bands in both the IR and Raman effects. This in-plane COH bend and the C-O stretch at 1208 cm^{-1} (which was derived from an x-sensitive ring mode) cause strong IR bands and strong-medium Raman bands.

The formyl modes comprise the CH stretch, the CO stretch, the in-plane HCO and CCO bends, the CH out-of-plane wag and the torsion. In vanillin these modes are credited with bands at 2722, 1669, 1399, 588, 1008, and 128 cm^{-1}. The CO stretching band and the C-CHO stretch at 1150 cm^{-1} (derived from an x-sensitive ring mode) are strong in both IR and Raman spectra. The remaining formyl modes are of weak-medium intensity.

The methoxyl modes include three CH stretches, three HCH bends, two OCH bends, one COC bend, one O-CH_3 stretch and two torsions. The C-OCH_3 stretching mode derived from an x-sensitive ring mode, the HCH bends, the COC bend and the A' OCH bend have strong IR bands and medium-strong Raman bands. The remaining modes are medium-weak in both the IR and Raman effects.

The assignments of the substituent modes in the IR spectra of lignins agree with those made for the analogous modes in vanillin.

SUMMARY

The interpretation of the vibrational spectra of vanillin presented in Chapter IV may be used to assign bands in the IR and Raman spectra of lignins. The substituent insensitive phenyl modes and the substituent modes of vanillin

should occur at approximately the same frequencies and intensities in the spectra of softwood lignins. Considering both their frequency shifts and their intensities, the CC stretching modes would be the easiest to identify in vibrational spectra of lignins. Cellulose spectra are relatively clear of bands above 1500 cm^{-1}, so lignin bands arising from modes 8a, 8b and 19a should be the easiest to discern in whole wood spectra.

The substituent sensitive phenyl modes of vanillin might also provide a clue to the origin of some of the bands in the spectra of lignins, though they may be somewhat shifted in frequency.

Based on the proposed vanillin assignments, several of the assignments contained in Hergert's review (123) are challenged. It is suggested that bands at 1270, 1230 and 1130 cm^{-1} in guaiacyl derivatives are not ring breathing modes coupled with CO stretching modes, as they were classified by Hergert. It is proposed that the bands at 1270 and 1230 cm^{-1} be attributed to CO stretching modes coupled with other substituent modes. And that the 1130 cm^{-1} band is due to an aromatic CH in-plane deformation. It is also proposed that the guaiacyl bands at 1160 and 1040 cm^{-1}, identified in Hergert's review as aromatic CH in-plane bending modes, are due to vibrations of the methoxyl group.

CONCLUSION

The vibrational spectra of phenol, benzaldehyde, anisole, 4-hydroxybenzaldehyde, guaiacol, m-anisaldehyde, and vanillin were assigned. Group frequency data, normal coordinate calculations, and information from the vibrational spectra were used to make the assignments. Modified valence force fields were used in the normal coordinate calculations. The force fields for these calculations were constructed from a phenyl force field and the appropriate substituent force fields. The initial force fields for the monosubstituted benzenes were refined to the observed frequencies. The observed frequencies of the monosubstituted derivatives were calculated with an average error of 4-6 cm^{-1}. The force constants from these refined fields were used to calculate the frequencies of the normal modes of the di- and trisubstituted benzenes. The observed frequencies of these compounds were calculated with an average error of 11-15 cm^{-1}. The reasonable fit of observed to calculated frequencies indicates that these force constants would be transferable to more complex lignin model compounds.

The effect of mono-, di- and trisubstitution on the frequencies and intensities of the fundamental modes of benzene were noted. Modes that shifted due to mono-, di- or trisubstitution were identified. Six of the thirty fundamental phenyl modes were found to be substituent sensitive in the monosubstituted benzenes. In the disubstituted compounds, twelve of the phenyl modes were classified as substituent sensitive. And in the trisubstituted benzene, sixteen of these modes were identified to be substituent sensitive. The magnitude of the shift was dependent on the nature of the substituent and, in the poly-substituted compounds, on the pattern of substitution on the ring. The modes whose frequencies were insensitive to substitution were also identified. There are few regularities in the intensities of the phenyl bands on going from mono- to trisubstituted

benzene derivatives. The intensities of these peaks can be explained to some extent based on knowledge of the form of the mode, the nature of the substituents and the pattern of substitution.

The behavior of the substituent modes on increased substitution of the ring was also noted. The frequencies and intensities of the substituent modes were found to be relatively insensitive to other substituents on the ring.

The results of this investigation, the substituent and phenyl force fields and the assignments for the model compounds, can be used to interpret the spectra of more complex lignin model compounds, and to gain some understanding of the vibrational spectra of lignins.

RECOMMENDATIONS FOR FUTURE WORK

There are two basic directions for future work in this area. One is to perform normal coordinate calculations for other lignin model compounds. The other is to begin systematically recording and analyzing the vibrational spectra of lignins, lignin model compounds and derivatives of these compounds.

Normal coordinate calculations can be used to analyze the vibrational spectra of slightly more complex lignin model compounds than those studied in this investigation. One class of compounds that should be investigated is 3,5-dimethoxy-4-hydroxy substituted benzenes, as model compounds for syringyl lignins. Since lignin is a polyphenyl compound, an analysis of some of the diphenyl lignin model compounds should also be studied. For example, it would be interesting to perform calculations for β-1 linked phenyl groups, looking at the effect changes in the angle between the planes of the two aromatic rings has on the coupling between the vibrations of the two rings and the calculated normal frequencies.

It would also be of interest to use the information gleaned from the analysis of the spectra of vanillin to begin to interpret the spectra of native lignins. For example, the two bands at 1600 cm^{-1} are due to planar vibrations of the ring. The frequencies of these bands are relatively substituent insensitive. Using the intensities of these bands in the spectra of woody cells, obtained with the Raman microprobe, it may be possible to gain information about the orientation of the benzene rings in native lignin.

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APPENDIX I

THE THEORY AND PRACTICE OF NORMAL COORDINATE ANALYSIS

A normal coordinate analysis uses a simplified model of a molecule to calculate the normal modes and frequencies with which this molecule vibrates. Comparison of this calculated spectrum to the observed vibrational spectra of the molecule is used to interpret the observed spectra. This appendix will briefly describe the simplified model and the calculations involved in a normal coordinate analysis. More detailed discussions of the theory underlying these calculations can be found in most texts on mechanics (129,130). The details of the application of this theory to molecular vibrations are given by Wilson, et al. (3). A series of articles by McIntosh and Michaelian (131) were written "to give the beginning vibrational spectroscopist a more complete introduction to the use of the Wilson GF matrix method". Discussions of the theory and practice of normal coordinate calculations can also be found in many of the texts on vibrational spectroscopy (e.g., 4,5). This discussion is based on that provided by Wilson, et al. in Molecular Vibrations (3).

THE MOLECULAR MODEL

The simplified model of the molecule used in normal coordinate calculations assumes the molecule to consist of atoms having all of their mass concentrated at a point. These point masses are held together by forces, which for purposes of visualization, may be thought of as weightless springs that approximately obey Hooke's law. The model should obey the laws of quantum mechanics.

CLASSICAL MECHANICAL DEVELOPMENT

A molecule consisting of N atoms can be completely described by 3N mass-weighted cartesian displacement coordinates, q_i. These coordinates are defined to be:

$$q_1 = \sqrt{m_1}\Delta x_1,\ q_2 = \sqrt{m_1}\Delta y_1,\ q_3 = \sqrt{m_1}\Delta z_1,\ q_4 = \sqrt{m_2}\Delta x_2,\ \text{etc.} \tag{1}$$

Using these coordinates, the kinetic energy of the molecule can be written as

$$2T = \sum_{i=1}^{3N} (dq_i/dt)^2 = \sum_{i=1}^{3N} \dot{q}_i^2 \tag{2}$$

The potential energy will also be a function of the displacements, q_i. For small displacements, the potential energy, V, can be expanded as a power series in the displacement q_i:

$$2V = 2V_o + 2 \sum_{i=1}^{3N} (\partial V/\partial q_i)_o\, q_i + \sum_{i=1}^{3N} (\partial^2 V/\partial q_i \partial q_j)_o q_i q_j + \cdots \tag{3}$$

The first term of this equation drops out if the zero of energy is chosen so that the energy of the equilibrium configuration is zero. The second term also drops out; when the q_i are zero, the molecule will be at equilibrium so the energy must be a minimum, therefore

$$(\partial V/\partial q_i)_o = 0 \qquad i = 1 \text{ to } 3N \tag{4}$$

For small atomic displacements, i.e., small q, terms greater than quadratic can be neglected. The equation for the potential energy reduces to:

$$2V = \sum_{i,j=1}^{3N} (\partial^2 V/\partial q_i \partial q_j)_o q_i q_j = \sum_{i,j=1}^{3N} f_{ij} q_i q_j, \tag{5}$$

where

$$f_{ij} = (\partial^2 V/\partial q_i \partial q_j)_o, \tag{6}$$

analogous to the expression for a harmonic oscillator. Substituting these expressions for the kinetic and potential energies [Eq. (2) and (5)] into Newton's equations of motion,

$$d(\partial T/\partial \dot{q}_j)/dt + \partial V/\partial q_j = 0 \qquad j=1,2,\ldots,3\underline{N} \tag{7}$$

results in a set of $3\underline{N}$ simultaneous second-order linear differential equations:

$$\ddot{q}_j + \sum_{i=1}^{3\underline{N}} f_{ij}\, q_i = 0 \qquad j = 1 \text{ to } 3\underline{N} \tag{8}$$

One solution for these equations is

$$q_i = A_i \cos(\lambda^{1/2} t + \varepsilon) \tag{9}$$

where A_i, λ, and ε are constants. Substitution of this solution into Eq. (8) yields a set of algebraic equations:

$$\sum_{i=1}^{3\underline{N}} (f_{ij} - \delta_{ij}\, \lambda)A_i = 0 \qquad j = 1 \text{ to } 3\underline{N} \tag{10}$$

where δ_{ij} is the Kronecker delta symbol. This is a set of $3\underline{N}$ simultaneous homogeneous linear equations. This set of equations can also be written in matrix form:

$$\begin{pmatrix} f_{11} - \lambda & f_{12} & \cdots & f_{13\underline{N}} \\ f_{21} & f_{22} - \lambda & \cdots & f_{23\underline{N}} \\ \cdots & \cdots & \cdots & \cdots \\ f_{3\underline{N}1} & f_{3\underline{N}2} & \cdots & f_{3\underline{N}3\underline{N}} - \lambda \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \\ \cdots \\ A_{3\underline{N}} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ \cdots \\ 0 \end{pmatrix} \tag{11}$$

For a nontrivial solution of this system to exist the determinant of the coefficients must be zero, i.e.,

$$\det \left| \underline{F} - \lambda\, \underline{E} \right| = 0 \tag{12}$$

where F is the matrix of the f_{ij}, and $\underline{E}$ is a unit matrix. This is called the characteristic equation or secular equation of matrix (11). Solving for λ gives the eigenvalues for Eq. (10). In this problem the eigenvalues, λ, are related to the fundamental frequencies of vibration of the molecule,

$$\upsilon = \lambda^{1/2}/2\pi \tag{13}$$

Substitution of an eigenvalue into the set of linear equations determines the eigenvector or normal mode for this frequency. The normal modes of vibration of a system of masses, such as a molecule, are the characteristic vibrations of the system. All motions of the system can be expressed as linear combinations of these normal modes. The eigenvalues, or normal frequencies, are the frequencies of the normal modes of vibration. Normal modes are also referred to as normal vibrations, fundamental modes, fundamentals, or characteristic modes or vibrations.

These eigenvectors are linearly independent, and can be used to determine a new coordinate system for the molecule called normal coordinates. Each eigenvector corresponds to a normal coordinate, Q_k. In this new coordinate system the potential energy expression contains only squares of the normal coordinates, no cross products. That is, the potential energy matrix will be a diagonal matrix with no off-diagonal terms. The expressions for the kinetic and potential energies in normal coordinates are (3):

$$2T = \sum_{k=1}^{3N} \dot{Q}_k^2 \qquad\qquad 2V = \sum_{k=1}^{3N} \lambda_k Q_k^2 \tag{14}$$

Substitution of these expressions for the kinetic and potential energies into the time independent Schrodinger wave equation is the basis of the quantum mechanical development. In normal coordinates the wave equation is separable into $3N-6$ equations, one for each normal coordinate. Each of these equations is a differential equation in one variable, the wave equation for the linear harmonic oscillator. For details of this development see Chapter 3 of Molecular Vibrations (3).

INTERNAL COORDINATES

Internal coordinates, rather than cartesian coordinates, are usually used in normal coordinate analyses. Internal coordinates use changes in bond lengths and bond angles to describe the relative postions of the atoms in the molecule. These coordinates are unaffected by translations and rotations of the molecule as a whole. This coordinate system is the most physically significant set for use in describing the potential energy of the molecule; it associates the force constants with particular chemical bonds or groups.

Only five different types of internal coordinates are needed to completely represent any given vibration of a molecule. These are bond stretching, valence angle bending, out-of-plane wag (the deformation of the angle between a bond and a plane defined by two bonds), torsion (the change in the dihedral angle between the planes defined by the first three and the second three atoms of four atoms bonded in sequence is considered to be the torsion about the bond between the middle two atoms), and linear valence angle bending. In terms of internal coordinates the kinetic energy expression can be written

$$2T = \dot{\underline{R}}'\underline{G}^{-1}\dot{\underline{R}} \tag{15}$$

where $\dot{\underline{R}}$ is the matrix of the time derivatives of the internal coordinates, $\dot{\underline{R}}'$ is the transpose of matrix $\dot{\underline{R}}$, and $\underline{G}^{-1}$ is the inverse of the $\underline{G}$ matrix, which is defined to be:

$$\underline{G} = \underline{B}\underline{M}^{-1}\,\underline{B}' \tag{16}$$

In this equation $\underline{B}$ is the transformation matrix from cartesian coordinates to internal coordinates, and $\underline{M}^{-1}$ is the inverse of the diagonal matrix $\underline{M}$ formed from the masses of the constituent atoms.

The potential energy expression in internal coordinates becomes

$$2V = \underline{R}'\underline{F}\underline{R} \tag{17}$$

where $\underline{F}$ is the matrix of force constants for the molecules with

$$f_{ij} = (\partial^2 V/\partial r_i \partial r_j)_o \tag{18}$$

In this expression r_i and r_j refer to internal coordinates. These equations for V and T lead to a secular equation of the form

$$\left| \underline{GF} - \underline{E}\,\lambda \right| = 0 \tag{19}$$

which is analogous to Eq. (12). A normal coordinate analysis then, consists of constructing the $\underline{G}$ and $\underline{F}$ matrices and solving the secular equation for the normal frequencies, which in turn are used to determine the normal modes and coordinates.

There is no unique way to define a set of internal coordinates for a molecule. When defining a set of internal coordinates all changes in bond length are usually chosen first. Then as many changes in bond angles as are necessary to complete a set of $3\underline{N}-6$ coordinates ($3\underline{N}-5$ for linear molecules) and sufficient to describe all possible deformations are added. The angles that are included in this set should be independent. However, it is often necessary to include redundant coordinates to take advantage of the symmetry of the molecule. When this is done, the number of internal coordinates exceeds the number of normal modes by the number of redundant coordinates. These additional coordinates correspond to zero vibrational frequencies. Usually these redundancies can be removed once the problem is transformed to symmetry coordinates (see section on symmetrization for discussion of symmetry coordinates). In cyclical structures

though, a certain number of redundancies arise from the ring structure and cannot be eliminated by anything save full diagonalization. In these cases it is important to be aware of the linearly dependent nature of the coordinates and recognize that unique, independent values for the force constants will not be determined.

G-MATRIX

In cartesian displacement vectors, X, the kinetic energy expression is written:

$$2T = \dot{\underline{X}}'\underline{M}\dot{\underline{X}} \tag{20}$$

Defining $\underline{B}$ as the transformation matrix from cartesian coordinates to internal coordinates,

$$\underline{R} = \underline{B}\underline{X} \tag{21}$$

and

$$\dot{\underline{R}} = \underline{B}\dot{\underline{X}} \tag{22}$$

Left multiplying both sides by $\underline{B}^{-1}$,

$$\dot{\underline{X}} = \underline{B}^{-1}\dot{\underline{R}} \tag{23}$$

Substituting this equation into the kinetic energy expression,

$$2T = \dot{\underline{R}}'\underline{G}^{-1}\dot{\underline{R}} \tag{24}$$

where

$$\underline{G}^{-1} = \underline{B}'^{-1}\underline{M}\underline{B}^{-1} \tag{25}$$

or

$$\underline{G} = \underline{B}\underline{M}^{-1}\underline{B}' \tag{26}$$

The $\underline{G}$ matrix is constructed from the transformation matrix $\underline{B}$ and the inverse of the diagonal matrix of the atomic masses. The Wilson S vector technique (3) is

used to determine the transformation matrix $\underline{B}$ from known or assumed atomic positions.

$\underline{F}$-MATRIX

The potential energy expression in internal coordinates is:

$$2V = \underline{R}'\underline{F}\underline{R} \tag{27}$$

$\underline{F}$ is the matrix of force constants, f_{ij},

$$f_{ij} = (\partial^2 V/\partial r_i \partial r_j)_o \tag{28}$$

The diagonal force constants, i.e., i=j describe the deformation of the individual internal coordinates. The off-diagonal terms, or interaction constants [$i \neq j$ in Eq. (28)] represent the interaction between two different internal coordinates. The $\underline{F}$ matrix is a symmetric matrix ($f_{ij} = f_{ji}$). Unlike the $\underline{G}$ matrix, the $\underline{F}$ matrix cannot readily be calculated from experimental data. The only convenient source of information about these force constants is the vibrational spectrum. If the normal frequencies of vibration of a molecule are known, they can be used to calculate the force constants of the molecule. However, only for a diatomic molecule is this sufficient to completely determine the full quadratic force field. In order to determine the force constants from the vibrational spectrum it is necessary to make certain simplifying assumptions about the nature of the potential energy matrix. This is usually accomplished by using an approximate force field. Many different approximate force fields have been tried, no one simplification being best in all situations.

One such approximate force field is known as a valence force field (VFF). This approximation considers the potential energy to arise from the stretching

of bonds and the deformation of bond angles, interaction between nonbonded atoms are not directly considered. In other words, only the diagonal elements of the F matrix are considered. The VFF gives only a rough approximation to the frequencies (or force constants).

The force field used in this investigation is called a modified valence force field (MVFF). The force field is intermediate between a VFF and a full or general quadratic force field (GQFF). A MVFF is developed by adding a few judiciously chosen interaction constants to a VFF. This could also be viewed as setting negligible interaction force constants in a GQFF to zero. Physically, the addition of interaction force constants amounts to taking into consideration the change in the stiffness of a bond due to the distortion of other bonds (3). Another assumption that the MVFF makes is that similar force constants can be grouped together by assigning one common numerical value. In the calculations this is facilitated by calculating the F matrix indirectly. A transformation matrix, Z , is used to calculate the F matrix from the numerical values of the force constants:

$$f_{ij} = z_{ijk}\phi_k \tag{29}$$

where f_{ij} is an element of the F matrix and ϕ_k is the numerical value of the force constant.

SYMMETRIZATION

Another way to reduce the size of the F matrix is to utilize the symmetry of the molecule. The symmetry of many compounds allows their F and G matrices to be factored into a number of smaller matrices. In addition, knowledge of just the geometry (and therefore the symmetry) of a molecule permits the determination of the number of fundamental modes, their Raman and IR activity, the

degrees of the factors of the secular equation (sizes of the smaller matrices), the polarization properties of the Raman lines and other useful information. This all results from the application of group theory to the symmetry elements of molecules. The theory and applications of group theory are either the subject of, or discussed in many texts (e.g., 3,132-134). Those areas pertinent to this study will be briefly discussed in this section.

The symmetry of any molecule can be completely described by four symmetry elements: proper rotation axes, reflection planes, improper rotation axes (a proper rotation axis coupled with a reflection plane), and a center of inversion. Each of these symmetry elements has associated with it a symmetry operation: rotation about the axis, reflection through the plane, improper rotation about the axis (rotation about the axis followed by reflection through the plane, or vice versa), and inversion through the center, respectively. The symmetry element is the geometrical entity with respect to which the symmetry operation is carried out.

A molecule can have any, all, or none of these symmetry elements. For any of these elements to be present in the molecule, the symmetry operation associated with the symmetry element must take the molecule into an equivalent configuration, one that is indistinguishable from the original. For example, benzene has proper axis of rotation perpendicular to the plane of the ring, coincident with the center of mass of the ring (Fig. 31). Rotation by $\pi/3$ about this axis results in an equivalent configuration, distinguishable from the original only by arbitrary numbering. Benzene is a highly symmetric molecule, in addition to the sixfold axis of rotation, C_6, it also has six twofold axes of rotation perpendicular to the sixfold axis, $3C_2'$ and $3C_2''$, a reflection plane

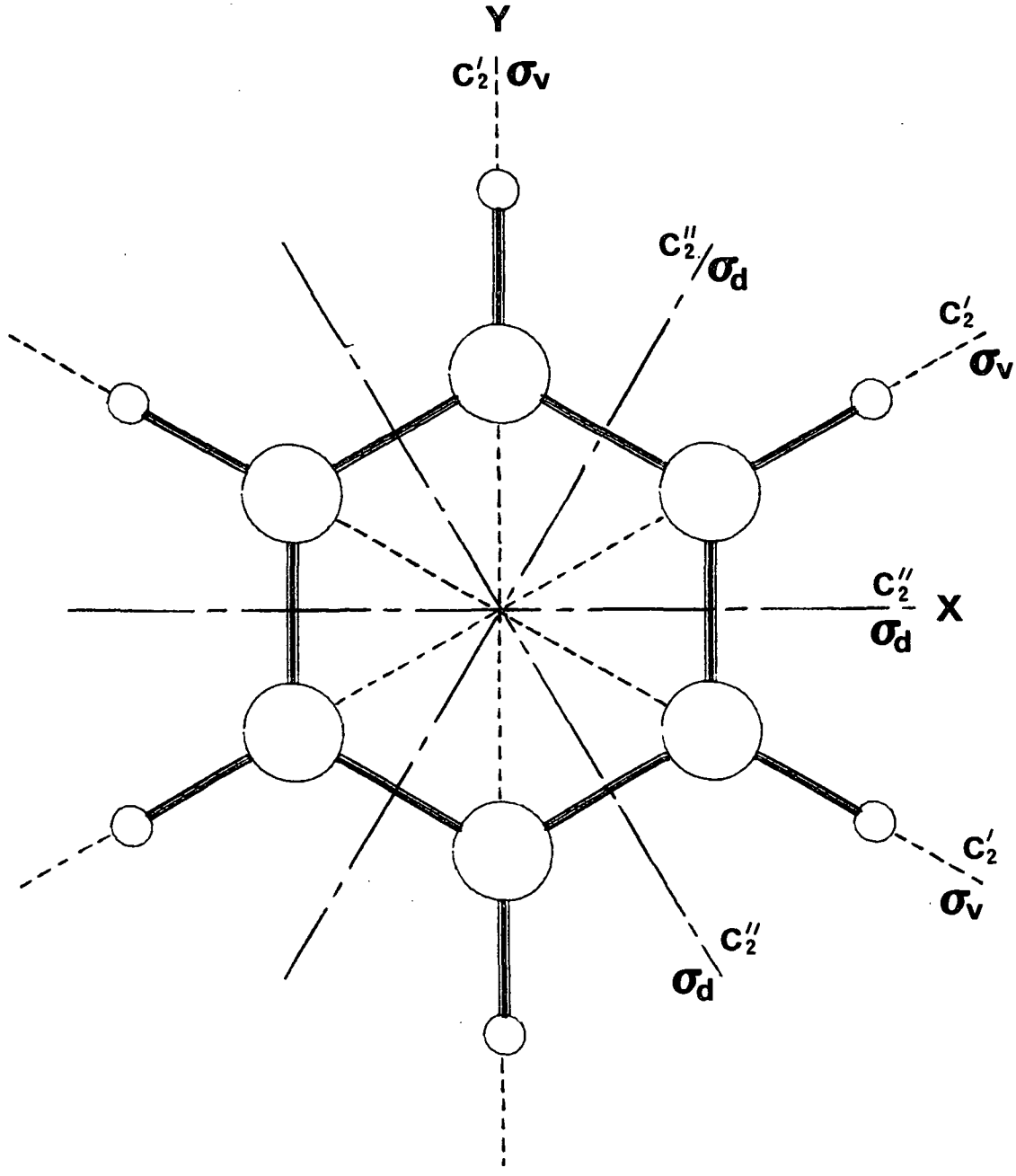


Figure 31. The symmetry elements of benzene. The C_6 axis is perpendicular to the plane of the ring and passes through the center of the ring The σ_h reflection plane is coincident with the plane of the ring.

coincident with the ring, σ_h, six reflection planes coincident with the six two-fold axes of rotation, $3\sigma_v$ and $3\sigma_d$, an improper axis of rotation coincident with the sixfold axis of rotation, S_6, and a center of inversion, i. The addition of unsymmetrical substituent groups reduces the symmetry of the ring. The model compounds included in this investigation have only a single plane of reflection, coincident with the aromatic ring. In addition to the symmetry operations defined above, an identity operation, E, is included when determining the set of symmetry operations for a molecule. Execution of the identity operation leaves the molecule unchanged.

A mathematical group is defined to be a collection of elements which have the properties of closure, associative, inverse and identity when combined. A complete set of symmetry operations for any molecule constitutes a mathematical group. These groups, referred to as point groups, are categorized by the symmetry operations they encompass. For example, the point group consisting of just the identity operation and a plane of reflection is represented by the symbol C_S. The model compounds in this thesis all have C_S symmetry. Benzene, and any other molecule possessing the symmetry operations identified for benzene, belong to the D_{6h} point group. Descriptions of other point groups can be found in any discussion of the chemical applications of group theory.

The symmetry elements of a molecule can also be used to classify the normal vibrations of a molecule. The vibrations are classified according to their behavior with respect to the symmetry elements of the molecule. These classifications are generically referred to as symmetry species. Each group has a characteristic number of symmetry species (equal to the number of classes of symmetry operations). In phenol, the normal modes of vibration can either be

symmetric or antisymmetric with respect to the plane of symmetry. Those modes which are symmetric with respect to the plane of symmetry belong to the A' symmetry species, those which are antisymmetric belong to the A" symmetry species. In benzene, those normal modes that are symmetric with respect to all of the symmetry elements belong to the A_{1g} symmetry species; those that are symmetric with respect to all of the symmetry elements but are antisymmetric with respect to the six twofold axes and the six reflection planes perpendicular to the ring, belong to the A_{2g} symmetry species; etc. The symmetry species and the number of normal modes represented by each are listed in Table LI for benzene and the model compounds.

The behavior of the normal modes with respect to the symmetry elements is used to determine which modes are IR active, which are Raman active, and which will have bands that are polarized in the Raman effect. Infrared activity is based on a change in the dipole moment of the molecule. A fundamental is IR active if it belongs to the same symmetry species as any of the components (x, y, and z) of the oscillating electric vector of the molecule. Raman activity results from a change in the polarizability of a molecule. A fundamental is Raman active if it belongs to the same symmetry species as any of the components of the polarizability tensor of the molecule. All fundamental modes of molecules belonging to the C_S point group are both IR and Raman active. The activity of the modes of benzene and the model compounds are summarized in Table LI. A '+' indicates activity, a '-' indicates that the mode is not active. The Raman active modes that are totally symmetric, i.e., symmetric relative to all symmetry elements in the molecule, are polarized. In benzene, the modes belonging to the symmetry species A_{1g} are polarized. In the other model compounds, the A' modes are polarized. A band is said to be polarized when the ratio of the intensity

of scattered light polarized in a plane perpendicular to that of the incident light to the intensity of scattered light polarized in the same plane as the incident beam is less than 0.75.

TABLE LI

POINT GROUP, SYMMETRY SPECIES, IR AND RAMAN ACTIVITY AND NORMAL MODES OF MODEL COMPOUNDS AS DETERMINED BY GROUP THEORY

Compound	Point Group	Symmetry Species	Raman Activity[a]	Infrared Activity[a]	Normal Modes
Benzene	D_{6h}	A_{1g}	+	-	2
		A_{2g}	-	-	1
		B_{1g}	-	-	-
		B_{2g}	-	-	2
		E_{1g}	+	-	1
		E_{2g}	+	-	4
		A_{1u}	-	-	-
		A_{2u}	-	+	1
		B_{1u}	-	-	2
		B_{2u}	-	-	2
		E_{1u}	-	+	3
		E_{2u}	-	-	2
Phenol	C_S	A'	+	+	23
		A''	+	+	10
Benzaldehyde	C_S	A'	+	+	25
		A''	+	+	11
Anisole	C_S	A'	+	+	28
		A''	+	+	14
4-Hydroxybenz-aldehyde	C_S	A'	+	+	27
		A''	+	+	12
Guaiacol	C_S	A'	+	+	30
		A''	+	+	15
m-Anisaldehyde	C_S	A'	+	+	32
		A''	+	+	16
Vanillin	C_S	A'	+	+	34
		A''	+	+	17

[a] '+' designates an active mode, '-' denotes an inactive mode.

In addition to elucidating various aspects of the vibrational spectra of molecules, the symmetry of the molecule can be used to block factor the $\underline{F}$ and $\underline{G}$ matrices. These matrices can be factored so that only the modes that belong to a certain symmetry species are represented in that block. For example, in the model compounds the $\underline{F}$ and $\underline{G}$ matrices can each be factored into two smaller matrices, one containing information on the A' modes, the other representing the A" modes. Similarly, the potential and kinetic energy matrices for benzene can be factored into ten blocks, the largest of which is the E_{2g} block with a dimension of four (see Table LI). Block factored matrices can be separated into their component matrices. Each of these blocks can be treated independently. So rather than solve the 30 x 30 secular equation for benzene, this can be factored into ten smaller problems, the largest having a 4 x 4 matrix.

The $\underline{F}$ and $\underline{G}$ matrices are factored by transforming from internal coordinates to symmetry coordinates. Symmetry coordinates are linear combinations of internal coordinates constructed by application of the projection operators of the symmetry species to the internal coordinates [for details, see (3,132-134)]. The resulting symmetry coordinates each belong to a symmetry species. In matrix notation, the transformation from internal to symmetry coordinates is:

$$\underline{S} = \underline{UR} \tag{30}$$

where $\underline{S}$ and $\underline{R}$ are the column vectors of the symmetry and internal coordinates, respectively, and $\underline{U}$ is the transformation matrix. The $\underline{F}$ and $\underline{G}$ matrices are factored by the application of this matrix:

$$\hat{\underline{G}} = \underline{UGU'} \tag{31}$$

and

$$\hat{\underline{F}} = \underline{UFU'} \tag{32}$$

or, in these calculations,

$$\hat{Z} = UZU' \tag{33}$$

and

$$\hat{F} = Z\phi \tag{34}$$

where $\hat{F}$, $\hat{G}$, and $\hat{Z}$ are the factored matrices.

SOLUTION OF THE SECULAR EQUATION

Solving the secular equation is an eigenvalue problem. Solution for a system of more than three equations is most easily effected by diagonalization of the GF matrix. The diagonal elements of the resultant matrix will be the eigenvalues or normal frequencies in this problem. Theoretically, the diagonalization of the GF matrix is effected by a transformation from internal coordinates to normal coordinates. The transformation matrix, L, is the matrix of the eigenvectors, or normal modes of vibration.

In these calculations, diagonalization of the GF matrix is achieved by successive Schmidt orthogonalization of the G and F matrices followed by Jacobi diagonalization. Schmidt orthogonalization is an algorithm which computes the transformation to a new set of coordinates in which G is a unit matrix. This transformation is then applied to the F matrix. The resultant matrix, H, is symmetric. H is diagonalized by the Jacobi method. Jacobi diagonalization is an algorithm that is based on the theorem: if H is symmetric, there exists an orthogonal matrix, S, such that S ' HS is a diagonal matrix whose diagonal elements are the characteristic roots of H. This and other methods used to solve the secular equation are described by Wilson, et al. (3) and by Schachtschneider (135).

The matrix of the normal modes, $\underline{L}$, can be used to calculate the potential energy distribution. The expression for the contributions of each internal coordinate to the potential energy is:

$$P.E.q_i = L_{ik}^2 F_{ii}/\lambda_k \qquad (35)$$

for the diagonal terms of $\underline{F}$. This equation describes the relative contributions of the i^{th} internal coordinate to the k^{th} normal mode. The potential energy distribution of a molecule gives an indication of the form of the various normal modes.

OPTIMIZATION OF THE FORCE CONSTANTS

The number of force constants generally exceeds the number of observed frequencies, even in simplified force fields. The values of these force constants therefore cannot be determined directly from the experimental data. In this thesis, initial values of the force constants are assumed, and then refined to minimize the difference between the calculated and observed frequencies. The resulting force field is not necessarily unique, but it can provide a good description of the molecular vibrations. Since the force constants are not uniquely determined, an analysis of the force constant errors is not discussed. Furthermore, the errors calculated using the Fletcher-Powell method are only good approximations of the error if the number of perturbations in the refinement approaches the number of force constants refined (136). This was rarely the situation.

The chemical and thermodynamic properties of bonds with similar nuclear environments are known to be similar. Therefore it is expected that the forces resisting deformation of these bonds will be similar. This implies that force

constants ought to be transferable between similar molecules or between similar groupings in different molecules. And that force constants developed for simple systems can be used to elucidate the spectra of more complex systems (5). The initial values of the force constants assumed in this investigation were transferred from similar groupings in different molecules.

Improvements in this initial force field are effected using a nonlinear least squares refinement procedure developed by Fletcher and Powell (69). The force constants are successively adjusted by this algorithm to minimize the least squares difference between the observed and calculated frequencies. The refinement proceeds until the corrections to the force constants fall below a preset value, or the ratio of successive weighted sums of squares of the residuals increases beyond a given value. Descriptions of the application of this method to the vibrational problem can be found in Pitzner's thesis (136) and in papers by Gans (70,137,138).

COMPUTER PROGRAMS

In this investigation a series of computer programs was used to set up and solve the secular equation. The programs were originally published by Schachtschneider (135). They were modified for operation on the IBM 360/44 computer at IPC by Pitzner (136). Only minor modifications were needed in these programs for use on the Burroughs 6900 computer now available at IPC. Copies of the programs and instructions for their use on the IBM 360/44 were provided by Pitzner (136). Updated versions of the programs are stored on tape available at the computer center at IPC. Instructions for their use on the Burroughs 6900 are included in Appendix V.

Briefly, the principal programs used in these calculations were:

CART - With an input of atomic masses, bond lengths and bond angles, CART calculates the standard cartesian coordinates, moment of inertia tensor, center of mass coordinates, principal moments of inertia, and principal cartesian coordinates.

GMAT - Given the cartesian coordinates, atomic masses, internal coordinate definitions and symmetry transformation, GMAT calculates the B matrix, the G matrix, and the factored G matrix.

UBZM - For a SVQFF, the Z matrix is set up by UBZM from specification of the position of the F matrix elements (row and column numbers) and the number identifying each matrix element.

ZSYM - Given the Z matrix and the symmetry transformation, U , ZSYM factors the Z matrix.

FLPO - FLPO solves the secular equation by Schmidt orthogonalization followed by Jacobi diagonalization, and uses the Fletcher-Powell algorithm to refine an initial set of force constants to provide a nonlinear least squares fit of the calculated to observed frequencies. Input comprises the numerical values of the force constants, the Z and G matrices, and the observed frequencies. This program was constructed by Pitzner (136) from an IBM subroutine of the Fletcher-Powell method and Schachtschneider's FADJ program (135).

EIGV - Input of the force constant values, the Z, G, and B matrices, the atomic masses and cartesian coordinates is needed for EIGV to solve the secular equation and to compute the eigenvectors, the potential energy distribution, the

cartesian displacement coordinates and the mean square amplitudes for each normal mode.

PAMOLE - PAMOLE uses a plotter to draw three-dimensional "ball and stick" representations from the cartesian coordinates of the atom. The drawings can be made from any viewpoint and at any reasonable distance from the molecule. A variaton of this program is used to draw the displacements of the atoms from equilibrium in any normal mode. The program was written by Adamson (139) and modified for use on the IBM 360/44 computer and Calcomp 110 digital plotter by Pitzner (136). Significant revisions of this program were needed for it to run on the Burroughs 6900 using a Calcomp 1012 digital plotter.

APPENDIX II

ASSIGNMENT OF THE PHENYL MODES OF SUBSTITUTED BENZENES

Assignments have been proposed for the vibrational spectra of many substituted benzenes. Based on these assignments, substituent sensitive and substituent insensitive phenyl modes have been identified. As well, frequency ranges for each of the phenyl modes of mono-, di-, and trisubstituted benzenes have been proposed.

The behavior of the phenyl modes on mono-, di-, and trisubstitution, in general, is reviewed in this appendix. Wilson's notation for benzene normal modes will be used (Fig. 2). Benzene fundamentals are valid descriptions of the phenyl modes since the benzene nucleus dominates in the determination of the force field of the molecule.

MONOSUBSTITUTED BENZENES

The following discussion of the fundamental modes of monosubstituted benzenes is based on reviews by Varsanyi (6), Whiffen (21), Dollish (22) and Katritzky (23). The assignments discussed in this section are summarized in Table VI.

CH stretchings: 2, 7a, 7b, 20a, 20b

There are five CH stretching modes in monosubstituted benzenes. The frequencies of these modes lie in the range 2950-3120 cm^{-1}. None of the five modes are reported to be x-sensitive. Only one strong Raman band, and three IR bands are found in this region, though all five bands should be both Raman and IR active. The IR bands are generally assigned to 20b, 20a, and 2 in order of decreasing intensity (6). The Raman band has been assigned as mode 2. Several

summation bands can also appear in the same range as the CH stretching modes, leading to strong Fermi interactions, as in benzene itself (21).

CC Stretching Modes: 8a, 8b, 19a, 19b, 14

There are five CC stretching modes in monosubstituted benzene derivatives, all of which are relatively insensitive to substitution. The two frequencies of vibrational pair 8 are found close to the frequency of that benzene vibration, 1597 cm^{-1}. The e_{1u} degenerate vibration of benzene at 1486 cm^{-1} also splits into two bands (19a and 19b) that are close to the original benzene frequency. The frequency interval for 19a is proposed to be 1470-1515 cm^{-1}, and for 19b, 1440-1470 cm^{-1}. The 1310 cm^{-1} b_{2u} benzene ring stretch (vibration 14) is only slightly shifted upon substitution, and is found to lie in the range 1300-1350 cm^{-1}.

CH In-plane Bending Vibrations: 3, 9a, 15, 18a, 18b

Four of the five CCH in-plane deformations of monosubstituted benzene derivatives have very stable frequencies. The vibrations derived from 18a and 9a are almost unchanged from those of benzene, 1027-1032 cm^{-1} and 1170-1181 cm^{-1}, respectively. Modes 18a and 9a are the most intense of the CH in-plane deformation bands in the IR. Vibration 18a is also strong in the Raman, and is characteristic of monosubstitution (22). The band from mode 18b falls in the range 1065-1082 cm^{-1} and is very weak in intensity in both the Raman and IR. Vibration 15 lies between 1150 and 1160 cm^{-1}, and gives rise to a Raman band of medium intensity. The remaining in-plane CCH deformation, normal mode 3, has been assigned in the range 1253-1331 cm^{-1}. This band is very weak in both the IR and Raman spectra and is the least stable of these five vibrations.

In-plane Ring Deformations: 1, 12, 6a, and 6b

Two of these in-plane modes are x-sensitive. The ring stretch derived from benzene vibration 1 at 994 cm^{-1} is substituent sensitive, and falls in the range 1060-1100 cm^{-1} for heavy substituents (> 25 amu) and in the range 620-830 cm^{-1} for light substituents (< 25 amu) (6). The frequency of vibration 6a is also variable, with ranges of 300-530 cm^{-1} for light substituents and 650-710 cm^{-1} for heavy substituents. The other component of this e_{2g} benzene vibration, 6b, is scarcely changed in frequency and found to lie between 605 and 630 cm^{-1}. Vibration 12 gives rise to an intense Raman band in the range 990-1010 cm^{-1}. This mode is also fairly independent of monosubstitution.

Out-of-plane CH Deformations: 5, 10a, 10b(17b), 11 and 17a

Varsanyi (6) assigned a b_2 monosubstituted benzene mode to benzene vibration 10b for light substituents but to vibration 17b for heavy substituents. Whiffen (21) made no such distinction. None of these bands are particularly sensitive to monosubstitution. The ranges for these vibrations have been established as 728-797 cm^{-1} for mode 11, 824-847 cm^{-1} for mode 10a, 882-938 cm^{-1} for mode 10b(17b), 952-975 cm^{-1} for mode 17a, and 970-1000 cm^{-1} for mode 5. The out-of-plane hydrogen bending IR bands between 675 and 900 cm^{-1} have been found to be useful in substitution studies (140). Each number of adjacent hydrogen atoms generates a unique combination of strong IR bands in this region. Five adjacent hydrogen atoms on the ring (monosubstituted benzenes) generally give rise to strong IR bands at 700 cm^{-1} and 740 cm^{-1}. Four adjacent hydrogen atoms (o-disubstituted benzenes) generate a stong IR band at 750 cm^{-1}, etc.

Out-of-plane Ring Deformations: 4, 16a and 16b

The out-of-plane ring vibrations are also relatively independent of substitution. Departures of the two components of the e_{2u} benzene vibration 16 are

small, vibration 16a appearing in the range 390-420 cm^{-1}, and vibration 16b at 430-560 cm^{-1}. The strongest of these bands, vibration 4 occurs as an intense IR band at 680-700 cm^{-1}. All of these bands are weak in the Raman effect. Whiffen (21) considered mode 16b to be substituent sensitive.

X-sensitive Vibrations: 9b, 13(7a) and 17b(10b)

There are six vibrational modes in which the substituent moves with significant amplitude, giving rise to frequencies which are sensitive to the mass of the substituent. In addition to the three modes discussed above, modes 1, 6a, and 3(16b), there is a CX in-plane bending mode, 9b, a CX stretching mode, 13(7a), and a CX out-of-plane deformation 17b(10b) (6) that are considered to be X-sensitive. The CX in-plane bending mode is generally weak in the Raman spectrum. The frequency depends on both the mass and the binding strength of the substituent to the ring. The frequency range for this vibration extends from 200 cm^{-1} to 410 cm^{-1}. Varsanyi (6) relates the CX stretching vibration to benzene vibration 13 for light substituents and to vibration 7a for heavy substituents. Mode 13 is found to lie between 1100 and 1280 cm^{-1} and is influenced by the extent of conjugation with the substituent. Mode 7a is found in the range 260-420 cm^{-1}. Whiffen (21) assigned the CX stretching mode to vibration 13. The CX out-of-plane deformation falls between 140 and 250 cm^{-1}. The frequency is determined principally by mass and bonding strength, but can be influenced by coupling effects. Varsanyi assigned this mode in the monosubstituted derivatives to benzene vibration 17b for light substituents and 10b for heavy substituents. Again, Whiffen did not make a distinction, assigning the CX out-of-plane bending band to mode 17b. Whiffen did not consider vibration 3 to be an x-sensitive mode, but instead included vibration 16b.

DISUBSTITUTED BENZENES

The effect of disubstitution on the fundamental modes of benzene has been the subject of a number of papers. Green reviewed the behavior of the benzene fundamentals in disubstituted benzenes containing only methyl and halogen substituents (93-95). Bogomolov classified the vibrations of disubstituted benzenes based on their specificity to the frequency and form of the analogous benzene modes (96-98). Katritzky discussed the positions and intensities of nine characteristic bands of disubstituted benzenes based on the vibrational spectra of a large number of compounds (99-101). In his review of the vibrational spectra of benzene derivatives Varsanyi (6) discussed the appearance of the benzene fundamentals in ortho-, meta-, and para-disubstituted benzene derivatives. Bellamy summarizes the behavior of a number of vibrations on disubstitution in his review of the IR spectra of benzene derivatives (82). These studies form the basis for the following discussion of the phenyl modes of disubstituted benzenes.

p-Disubstituted Benzenes

CH Stretching Vibrations: 2, 7b, 20a, 20b

Vibration 7b, generally found between 3030 and 3050 cm^{-1}, is weak in the IR absorption and depolarized in the Raman effect. Vibration 2 is also weak in the IR spectrum, but strong and polarized in the Raman spectrum, appearing between 3050 and 3085 cm^{-1}. The medium intensity IR band for mode 20a occurs in the interval 3050-3090 cm^{-1}, usually on the high frequency side of vibration 2. Vibration 20b was given a frequency interval of 3020-3120 cm^{-1}. Its position is roughly a function of the inductive effect of the substituents (6). Overall, these frequencies are considered to be rather independent of substituent type.

CC Stretching Vibrations: 8a, 8b, 19a, 19b, 14

The frequencies of vibrations 8a and 8b are not particularly x-sensitive. Mode 8a is found between 1570 and 1628 cm^{-1} and vibration 8b is found in the range 1552-1605 cm^{-1}. However, the intensities of these bands can be related to the nature of the substituent. The band intensities are lowered by substituents of the same chemical nature and increased by substituents of opposite character. The frequency of vibration 19a is found in a much higher frequency range than mode 19b, 1460-1530 cm^{-1} vs. 1370-1470 cm^{-1}. Mode 19b is generally weaker than mode 19a in IR spectra. The frequency domain of vibration 14 for phenols is 1330-1380 cm^{-1}, due to coupling of this ring mode with an OH deformation (102). Vibration 14 is generally thought of as an x-sensitive mode.

CH In-plane Bending Deformations: 3, 9a, 18a, 18b

Three of the CH in-plane bending vibrations, Nos. 9a, 18a, and 18b, are only slightly shifted from the positions of the corresponding modes in benzene, occurring in the ranges: 1158-1182 cm^{-1}, 1004-1022 cm^{-1}, and 1100-1128 cm^{-1}, respectively. The intensity of vibration 9a increases with an increase in the difference between the chemical natures of the two substituents. The intensity of vibration 18b is increased by electron-attracting substituents. Vibration 3 has a frequency range of 1260-1313 cm^{-1}. It is generally a weak IR band and is frequently impossible to identify (6).

In-plane Ring Deformations: 1, 12, 6a, 6b

Vibration 6b is the only one of the in-plane ring deformations to be essentially insensitive to p-disubstitution, occurring in the range 623-650 cm^{-1}. The other three modes are somewhat dependent on the mass of the two substituents. For two light (< 25 amu) substituents, mode 1 lies between 720 and 860 cm^{-1}, mode 12 appears in the range 680-760 cm^{-1}, and vibration 6a occurs between

330 and 480 cm^{-1}. If the masses of the two light substituents differ, the frequency of mode 1 is influenced by the lighter substituent, whereas modes 12 and 6a are influenced by the heavier substituent. For two heavy substituents, vibration 1 occurs in the 1040-1100 cm^{-1} interval, vibration 12 between 1060 and 1100 cm^{-1} and vibration 6a in the range 680-840 cm^{-1}. If the masses of these two heavy substituents differ, the position of vibration 1 is determined by the heavier substituent, and both modes 12 and 6a are influenced by the lighter substituent. If there is one light and one heavy substituent, the frequency ranges for vibration 1, 12, and 6a are: 1050-1100 cm^{-1} 481-680 cm^{-1} and 680-840 cm^{-1} respectively. In p-disubstituted phenols, vibration 1 was found to remain relatively constant between 825 and 857 cm^{-1} (102).

Out-of-plane Ring Deformations: 4, 16a, 16b

The three out-of-plane ring deformations are relatively stable. The frequency interval for vibration 4 has been found to be 665-735 cm^{-1} (687-711 cm^{-1} for p-substituted phenols). The two components of the e_{2u} vibration, mode 16 in benzene, should not be greatly shifted for p-disubstituted benzene derivatives. Mode 16a is found to be very stable at ca. 400 cm^{-1} and vibration 16b is found in the range 410-550 cm^{-1}.

Out-of-plane CH Deformations: 10a, 10b(5), 17a, 11(17b)

The out-of-plane CH deformations for p-disubstituted benzene derivatives were assigned to vibrations 10a, 10b, 17a and 11 for two light substituents, and to vibrations 10a, 5, 17a and 17b for two heavy substituents, by Varsanyi. Vibrations 10a and 11(17b) are found in the range 800-880 cm^{-1}. Vibrations 17a and 10b(5) are found in the interval 920-970 cm^{-1}. If using the out-of-plane hydrogen bending bands to identify the pattern of substitution, a strong IR band

at 820 cm^{-1} indicates two adjacent hydrogen atoms on the ring (140), as in p-disubstituted benzenes.

X-sensitive Modes: 9b, 15, 7a, 13(20a), 5(10b), 17b(11)

In addition to the x-sensitive modes discussed above, Varsanyi identifies two CX in-plane bending vibrations, 9b and 15, two CX stretching vibrations, 7a and 13(20a), and two out-of-plane CX deformations, 5(10b) and 17b(11) to be x-sensitive. The CX in-plane bending vibrations 9b and 15 have intervals of 255-460 cm^{-1} and 190-350 cm^{-1}, respectively. When the two substituents differ, vibration 9b is determined by the lighter substituent and vibration 15 by the heavier substituent. For two light substituents, the CX stretching vibrations are attributed to modes 7a and 13, and appear in the ranges 1100-1270 cm^{-1} and 1100-1320 cm^{-1}. For two heavy substituents these vibrations are assigned to modes 7a and 20a in the intervals 150-330 cm^{-1} and 360-550 cm^{-1}. And finally, for one light and one heavy substituent, the CX stretching modes are represented by modes 7a and 13 appearing at 240-400 cm^{-1} and 1100-1280 cm^{-1}. For two light substituents the out-of-plane CX deformations are attributed to vibrations 17b and 5. If there is at least one heavy substituent, these modes are assigned to vibrations 11 and 10b. Vibration 17b(11) appears in the range 80-220 cm^{-1}. Mode 5(10b) lies in the interval 240-380 cm^{-1}. The reactions of the phenyl modes to p-disubstitution are summarized in Table XXXI.

o-Disubstituted Benzenes

CH Stretching Vibrations: 2, 7a, 20a(13), 20b

In general, the CH stretching vibrations are considered to be independent of the type of substitution. The frequency interval of the CH stretching vibrations is 3000-3120 cm^{-1} in the spectra of all benzene derivatives. The four CH

stretching vibrations in o-disubstituted benzenes correspond to the benzene modes 2, 7a, 20a, and 20b for two light (< 25 amu) substituents. For two heavy (> 25 amu) substituents, Varsanyi considers the vibration identified as 20a to be better described by benzene mode 13. For mixed substitution this vibration corresponds to mode 20a.

CC Stretching Vibrations: 8a, 8b, 14, 19a, 19b

As in mono- and p-disubstituted benzene derivatives, the frequencies of the CC stretching vibrations are not shifted significantly by substitution on the phenyl ring. The frequency of vibration 8a is lower than that of 8b. Katritzky (101) gave the frequency ranges for these vibrations as 1577 ± 4 cm^{-1} and 1607 ± 9 cm^{-1}. He also noted that the IR band intensities for this pair of vibrations are lowered by substituents of the same chemical nature and increased by those of opposite character. Vibrations 19a and 19b are found in the frequency intervals 1430-1470 cm^{-1} and 1450-1520 cm^{-1}, respectively. The IR band intensities are found to be lower for substituents having acceptor characteristics. Donor substituents enhance the intensity of vibration 19b. The remaining CC stretching vibration, mode 14, can be strong in both the IR and Raman spectra. The frequency range for this vibration has been cited as 1250-1290 cm^{-1} for most substituents. In the spectra of o-substituted phenols this band is found above 1300 cm^{-1} (6).

CH In-plane Bending Vibrations: 3, 9b, 15, 18b

The frequencies of the CH in-plane bending vibrations 9b, 15, and 18b are insensitive to substitution, being only slightly shifted from their positions in unsubstituted benzene. The frequency of mode 3 is shifted on substitution, but is rather insensitive to the nature of that substitution, occurring in the range

1252-1292 cm^{-1}. This band is weak in both IR and Raman spectra. Vibration 15 is found between 1150 and 1168 cm^{-1} for most compounds. Its intensity in IR spectra is increased by substituents which are electron donors, or by two substituents of different natures. The IR intensity of vibration 18b is enhanced by halogen and electron-withdrawing substituents. This mode appears between 1011 cm^{-1} and 1056 cm^{-1}. Vibration 9b occurs within the range 1103-1148 cm^{-1}. Its IR intensity is weak.

In-plane Ring Deformations: 1, 6a, 6b, 12

In o-disubstituted benzene derivatives the in-plane ring deformations are substituent sensitive. Vibration 1 can occur in one of three frequency intervals. If both substituents are light it will occur in the range 630-780 cm^{-1}, if both are heavy, 1100-1130 cm^{-1}, or if one substituent is heavy and the other light it will appear between 1020 and 1070 cm^{-1}. Within these individual ranges the precise value of the frequency is determined by the total mass of the substituent, by the greater total mass in the case of mixed substituents. Vibration 12 has two frequency intervals, again depending on the mass of the substituents. If both substituents are light the frequency is found between 750 and 860 cm^{-1}, if both are heavy it appears in the range 1010-1050 cm^{-1}. For mixed substituents the mass of the lighter substituent determines the position of the band. The frequency range of vibration 6a is 560-600 cm^{-1} for two light substituents, and 640-720 cm^{-1} when at least one substituent is heavy. Vibration 6b is found below 560 cm^{-1} when at least one substituent is light. If both substituents are heavy this frequency is found between 650 and 750 cm^{-1}. The frequency is determined by the light substituent in mixed substitution. In Raman spectra vibration 6a is more intense.

Out-of-plane Ring Deformations: 4, 16a, 16b

For o-disubstituted benzene derivatives, the frequency interval of vibration 4 is 685-735 cm^{-1}. When there is a polyatomic substituent in which there is no free rotation about the bond to the aromatic ring (e.g., OMe or OEt groups) the frequency is high. The frequency range for vibration 16a has been determined to be 480-530 cm^{-1}, and that of vibration 16b as 410-470 cm^{-1}. Both of these bands are weak in the Raman.

Out-of-plane CH Deformations: 5, 11, 10a(17b), 10b(17a)

These four bands appear in the region 1000-650 cm^{-1}. Their position is principally determined by the number and position of substituents rather than the nature of the substituents. The strongest of these bands in the IR, which is generally the strongest IR band in this region, is used to identify the pattern of substitution. For o-disubstitution (four adjacent hydrogen atoms) this band is found in the range 770-735 cm^{-1} (82). This band is due to vibration 11. The frequency range cited for vibration 5 is 978-987 cm^{-1}. For light substituents the remaining two vibrations correspond to benzene modes 10a and 10b. For heavy substituents, these are better represented by modes 17b and 17a, respectively. These vibrations have been assigned to the intervals, 932-949 cm^{-1} and 841-864 cm^{-1}.

X-sensitive Modes: 9a, 18a, 7a, 13(7b), 17b(10a), 17a(10b)

In o-disubstitution the two in-plane CX bending modes are represented by vibrations 18a and 9a. Vibration 18a appears between 250 and 450 cm^{-1}. Vibraton 9a is found between 135 and 330 cm^{-1}. Its frequency is lowered for bulky substituents due to steric hindrance. Vibration 9a is usually more intense in the Raman spectrum than vibration 18a. The two in-plane CX stretching modes are described by vibrations 7a and 13 if at least one substituent is light, and by

vibrations 7a and 7b if both substituents are heavy. For two light substituents these vibrations are found in the ranges 1120-1340 cm^{-1} and 1080-1270 cm^{-1}, respectively. For two heavy substituents these ranges are considerably lower; vibration 7a is found in the interval 250-480 cm^{-1} and vibration 7b is located approximately 50 cm^{-1} lower. For mixed substituents the frequency interval of the carbon-heavy substituent stretch, vibration 7a, is 250-500 cm^{-1} and that of vibration 13, the carbon-light substituent stretch is 1100-1260 cm^{-1}. The two remaining X-sensitive modes are the CX out-of-plane bending vibrations. These correspond to modes 17b and 17a for two light substituents, and to 10a and 10b for two heavy substituents. The frequency interval of vibration 17b(10a) is 171-298 cm^{-1} and that of vibration 17a(10b) is 125-196 cm^{-1}. The frequencies of these modes for compounds with mixed substituents also fall into the ranges cited. Other x-sensitive modes, not specifically due to a motion of the CX bond, have been discussed in the previous sections.

m-Disubstituted Benzenes

CH Stretching Vibrations: 2, 7a(13), 20a, 20b

For light and mixed substituents the CH stretching vibrations are represented by benzene modes 2, 7a, 20a and 20b. For heavy substituents the mode corresponding to 7a is better described by benzene fundamental mode 13 (6). The frequency sequence of these vibrations has been observed to be 7a, 2, 20b and 20a, progressing toward higher frequencies. Normal mode 2 has been identified as the most intense line in the Raman spectra of these stretching vibrations.

CC Stretching Vibrations: 8a, 8b, 14, 19a, 19b

In m-disubstituted benzene derivatives, the frequency of vibration 8a is lower than that of vibration 8b, the ranges are: 1595-1575 cm^{-1} and 1600-1620.

It has been noted that the intensities of these bands in the IR are enhanced by substituents of the same chemical character, especially if electron-donating. The frequency of vibration 14 is found between 1300 and 1350 cm^{-1}. Modes 19a and 19b occur in the intervals 1430-1467 cm^{-1} and 1471-1495 cm^{-1}. Substituents having acceptor characteristics generally lower both the frequencies and the intensities of these bands. Donor substituents enhance the intensity of the higher frequency band. These five vibrations are relatively stable to substitution on the aromatic ring.

CH In-plane Bending Vibrations: 3, 9b, 18a, 18b

The in-plane CH bending vibrations correspond to benzene normal modes 3, 9b, 18a and 18b. The frequency ranges in which these vibrations typically occur are: 1262-1297 cm^{-1}, 1149-1166 cm^{-1}, 1061-1091 cm^{-1}, and 1082-1109 cm^{-1}, respectively. Vibration 3 is generally weak in IR spectra. The intensity of the band due to vibration 9b is increased by electron-donor substituents, and those of vibrations 18a and 18b are increased by electron-withdrawing substituents.

In-plane Ring Deformations: 1, 12, 6a, 6b

The in-plane ring deformation, vibration 1, has two frequency intervals in m-disubstitution. If both substituents are heavy, the vibration falls between 1050 and 1140 cm^{-1}. If at least one substituent is light this interval shifts to 650-750 cm^{-1}. This band is intense in both the Raman and IR effects. Vibration 12 is also intense in the Raman spectra, but medium in IR spectra. This band is relatively unaffected by m-disubstitution, appearing between 990 and 1010 cm^{-1}. For two light substituents, the frequency ranges of vibrations 6a and 6b are 450-550 cm^{-1} and 350-520 cm^{-1}. For two heavy substituents these frequencies occur in the intervals 640-710 cm^{-1} and 700-800 cm^{-1}, respectively.

For mixed substitution, the frequency of mode 6a is determined by the light substituent, while that of mode 6b is between 800 and 900 cm^{-1}. The Raman bands of vibration 6a are more intense than those of vibration 6b.

Out-of-plane Ring Deformations: 4, 16a, 16b

The frequency of vibration 4 is very stable in m-disubstitution, occurring between 675 and 700 cm^{-1}. Its IR band is very strong. The frequency ranges of vibrations 16a and 16b are 460-600 cm^{-1} and 400-490 cm^{-1}. The bands of both of these vibrations are weak in the Raman spectrum.

Out-of-plane CH Bending Vibrations: 5, 10a(17a), 10b(17b), 11

In m-disubstituted benzenes there is both an isolated ring hydrogen, and three adjacent ring hydrogens, each of which is responsible for a strong characteristic band in the 1000-650 cm^{-1} region of the IR spectrum. The three adjacent ring hydrogens are responsible for a strong band in the 750-810 cm^{-1} range, vibration 11. The isolated ring hydrogen gives rise to a band of medium strength in the region 860-900 cm^{-1}, vibration 10a(17a). The remaining two CH out-of-plane bending vibrations also occur in this frequency range, vibration 5 at 950-990 cm^{-1} and vibration 10b(17b) at 830-880 cm^{-1}. Vibrations 5, 10a, 10b and 11 describe the CH out-of-plane bending vibrations if both substituents are light. With heavy substituents these vibrations are better represented by benzene modes 5, 17a, 17b and 11. The position and number of substituents determines the frequency intervals of these vibrations. Within these ranges, the electron donating or accepting properties of the substituent determine the exact position of the band.

X-sensitive Vibrations: 9a, 15, 13(7a), 7b, 17a(10a), 17b(10b)

A number of the vibrations discussed under other headings are sensitive to substitution, however, not specifically due to vibrations of the C-X entity.

The vibrations discussed in this section are due to the motions of this group. Vibrations 9a and 15 describe the CX in-plane bending vibrations. Vibrations 13(7a) and 7b correspond to the CX stretching modes. Vibrations 17a(10a) and 17b(10b) are the out-of-plane bending motions of the CX bond for two light (heavy) substituent. Vibration 9a appears between 170-360 cm^{-1}. Its Raman band is stronger than the other CX in-plane bending vibration, mode 15. Vibration 15 falls in the range 260-480 cm^{-1}, occurring below 320 cm^{-1} when one of the substituents is electron attracting. In m-disubstitution by two light substituents, the CX stretching vibrations are modes 13 and 7b. The frequency range of vibration 13 is cited as 1120-1300 cm^{-1}, and that of 7b as 760-960 cm^{-1}. For two heavy substituents, modes 7a and 7b describe the CX stretches. Vibration 7a is found between 300 and 400 cm^{-1} and vibration 7b is found in about the same range, with the slightly higher upper limit of 430 cm^{-1}. For mixed substituents modes 13 and 7b again represent the CX stretches. Vibration 13 appears between 1100 and 1270 cm^{-1}, its exact position dependent on the chemical nature of the light substituent. Vibration 7b falls in the range 250-410 cm^{-1}; its precise position dependent on the mass of the heavier substituent. The frequency range for vibration 17a(10a) is 196-271 cm^{-1} and for 17b(10b) is 126-235 cm^{-1}.

TRISUBSTITUTED BENZENES

Relatively few studies have been made on trisubstituted benzenes. A discussion of the fundamental phenyl modes of trisubstituted benzenes is included in Varsanyi's review of the vibrational spectra of benzene derivatives (6). Bellamy summarizes the behavior of several of the fundamental modes of trisubstituted benzene derivatives (82). The following discussion of asymmetrically trisubstituted benzene derivatives is based primarily on these two works. The assignments discussed in this section are listed in Table XLIII.

Asymmetric Trisubstituted Benzenes

CH Stretching Vibrations: 2, 20a, 20b(13)

In asymmetric trisubstitution the CH stretching vibrations are normal modes 2, 20a and 20b. For three heavy substituents one of the CH stretching modes is classified as mode 13 rather than as mode 20b. The frequency interval of all CH stretching vibrations is 3000-3120 cm^{-1} in the spectra of benzene derivatives (6).

CC Stretching Vibrations: 8a, 8b, 14, 19a, 19b

As in m- and o-disubstitution, the frequency of vibration 8a will be lower than that of vibration 8b. The frequency ranges for these two modes are 1560-1610 cm^{-1} and 1571-1642 cm^{-1}. The frequency interval of vibration 14 is 1240-1290 cm^{-1}. Vibrations 19a and 19b are found in the ranges 1370-1450 cm^{-1} and 1460-1530 cm^{-1}, respectively. The frequencies of the CC stretching vibrations are relatively insensitive to substitution on the benzene ring. Their intensities, however, are dependent on the nature of the substituents and pattern of substitution.

CH In-plane Bending Vibrations: 3, 15, 18b

Vibrations 3, 15 and 18b are regarded as CH in-plane bending vibrations in asymmetric trisubstituted benzene derivatives. The frequency ranges for these vibrations are cited as 1260-1305 cm^{-1}, 1140-1170 cm^{-1} and 1070-1120 cm^{-1}, respectively.

In-plane Ring Deformations: 1, 12, 6a, 6b

The in-plane ring deformations, vibrations 1, 12, 6a and 6b are all sensitive to substitution to varying degrees. Their frequencies are influenced by the pattern of substitution and the mass of the substituents. For three light

substituents (< 25 amu), the frequencies of vibrations 1 and 12 appear below 1000 cm^{-1}. Vibration 1 has been assigned to the lower frequency range, 500-600 cm^{-1} and vibration 12 to 700-840 cm^{-1}. For three heavy substituents (> 25 amu), both of these frequencies appear above 1000 cm^{-1}. In this case, vibration 1 is assigned to the higher of the two frequency intervals and appears above 1100 cm^{-1}. Vibration 12 occurs above 1000 cm^{-1}. There are six possible substitution patterns of mixed light and heavy substituents. For all six cases, vibration 1 is expected to appear between 600 and 750 cm^{-1}. In four of these cases, vibration 12 is found in the same frequency ranges as it would be if all three substituents were heavy. In the remaining two cases it can drop below 600 cm^{-1} For three light substituents the frequency of 6a is found between 450 and 540 cm^{-1}, and that of 6b between 400 and 480 cm^{-1}. For three heavy substituents these ranges are shifted to 600-680 cm^{-1} and 700-800 cm^{-1}, respectively. In five of the six possible substitution patterns for mixed substituents, vibration 6a occurs between 600 and 750 cm^{-1}. In the remaining case, this band shows up below 450 cm^{-1}. Vibration 6b appears between 660 and 850 cm^{-1} for three of these cases, and below 450 cm^{-1} in the remainder. In vanillin, the substitution pattern is such that vibration 6a should occur between 600 and 750 cm^{-1}, and vibration 6b should appear in the interval 660-850 cm^{-1}.

Out-of-plane Ring Deformations: 4, 16a, 16b

Vibrations 4, 16a and 16b are the out-of-plane ring deformation. Vibrational pair 16 appears between 420 and 600 cm^{-1}. The frequency of vibration 16b falls between 428 and 476 cm^{-1}. Vibration 16a occurs at a higher frequency than 16a. No frequency range was cited for vibration 4.

Out-of-plane CH Bending Vibrations: 10a(5), 10b(17b), 11

The CH out-of-plane bending vibrations can be used to identify the pattern of substitution on the benzene ring, i.e., each substitution pattern has a unique sequence of bands in the 650-1000 cm^{-1} region of the infrared spectrum. In asymmetric trisubstitution there is an isolated ring hydrogen and a pair of adjacent ring hydrogens. Each type of hydrogen gives rise to a characteristic strong band in the IR. The two adjacent hydrogen bends give rise to a strong band between 800 and 860 cm^{-1}, vibration 11. The frequency of the band due to the isolated hydrogen (vibration 10b(17b)) is located between 860 and 900 cm^{-1}. The remaining vibration (mode 10a(5)) appears in the interval 920-970 cm^{-1}. Vibrations 10a, 10b and 11 denote trisubstitution by light substituents. Varsanyi uses vibrations 5, 17b and 11 to describe trisubstitution by heavy substituents.

Vibrations of the CX Bonds: 9a, 9b, 18a, 7a, 7b, 13(20b), 5(10a), 17a, 17b(10b)

In a trisubstituted benzene derivative there will be three CX in-plane bending vibrations: 9a, 9b and 18a, three CX stretching modes: 7a, 7b and 13(20b), and three CX out-of-plane bending vibrations: 5(10a), 17a and 17b(10b). The intervals of the CX in-plane bending vibrations overlap considerably. The frequency range of all three vibrations extends from 190 cm^{-1} to 390 cm^{-1}. For three light substituents the frequency interval for the CX stretching modes 7a, 7b and 13 are 1240-1310 cm^{-1}, 880-970 cm^{-1} and 1100-1210 cm^{-1}. For three heavy substituents, vibration 13 is better represented by mode 20b, and the frequency ranges become 300-460 cm^{-1}, 250-400 cm^{-1} and 350-580 cm^{-1}. For mixed substituents, there are six possible patterns of substitution, and four different combinations of frequency ranges and vibrations. For

vanillin, the substitution pattern is such that vibration 13 should appear between 1100 and 1210 cm^{-1}, and vibrations 7a and 7b should be found in the ranges 300-460 cm^{-1} and 250-400 cm^{-1}, respectively. The CX out-of-plane bending vibrations are assigned to modes 5(10a), 17a, and 17b(10b) for three light (heavy) substituents. The frequency ranges for these modes in asymmetric trisubstitution for light substituents are 190-270 cm^{-1}, 140-170 cm^{-1}, and 160-240 cm^{-1}; for heavy substituents they become: 200-310 cm^{-1}, 90-130 cm^{-1}, and 150-190 cm^{-1}, respectively.

APPENDIX III

RAMAN AND INFRARED SPECTRA FOR THE MODEL COMPOUNDS

TABLE LII

DEPOLARIZATION RATIOS - PHENOL(LIQUID)

Raman, cm^{-1}		Depolarization Ratio
242	m[a]	0.7
416	w	0.4
509	w	0.5
531	m	0.4
618	m	0.7
690	vw	
756	w	0.7
812	s	0.1
826	m	0.1
890	vw	0.7
958	vw	
986	m	
1001	vs	0.06
1026	s	0.07
1073	w	0.6
1154	m	0.6
1170	m	0.5
1192	w	
1220	sh	
1252	m	0.1
1380	w	
1470	w	0.6
1500	w	0.6
1594	m	0.7
1606	m	0.7
1622	vw	
3022	w	0.3
3061	w	0.2
3512	vw	

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

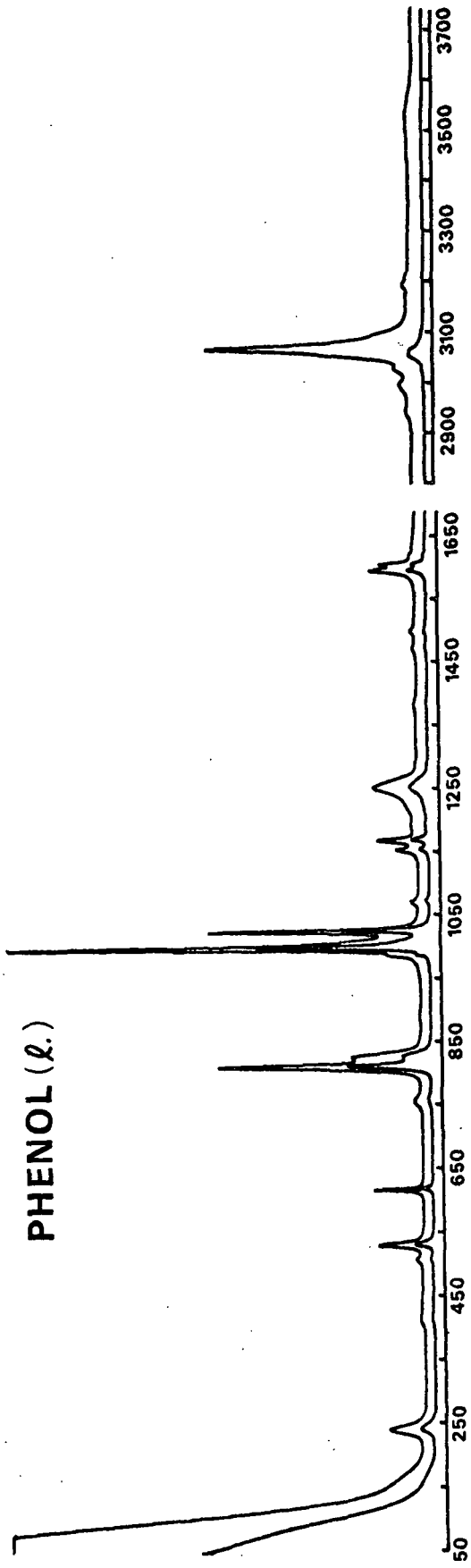


Figure 32. Raman spectra of phenol (ℓ) recorded with the analyzer parallel to the polarization of the incident light (upper) and perpendicular to the polarization of the incident light (lower).

TABLE LIII

SPECTRAL DATA - PHENOL IN CCl_4

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	434 sh[a]	1926 vw	
	527 m	1996 vw	
	615 m	2960 vw	
689 vs		3024 w	3022 vw
	810 s	3047 m	3040 sh
	825 m		3063 w
885 m		3077 w	
	986 sh	3093 w	3086 vw
1000 m	998 vs		3140
	1009 sh		3189
1025 m	1023 s	3346 m	
1070 m	1068 w	3610 m	3602 w
1106 m			
1152 m	1151 m		
1168 m	1167 m		
1181 s			
1222 s			
1256 s	1255 m		
1256 s	1255 m		
1313 w			
1342 m			
1361 m			
1386 w	(1374)		
1472 s			
1499 vs	1503 sh		
1521 vs			
1597 vs	1594 m		
1606 s	1600 m		
	1614 w		

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

TABLE LIV

SPECTRAL DATA - PHENOL IN CS_2 (IR) OR H_2O (RAMAN)

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	238 m[a]	3022 w	
	462 m	3043 m	
	531 m	3074 w	3066 w
	618 m	3089 w	
689 vs		3334 m	
752 vs		3346 w	
810 s	813 s	3589 m	
825 m			
883 m			
	987 m		
999 w	999 vs		
	1016 m		
1024 m	1025 s		
1069 m	1072 w		
1151 m	1155 m		
1167 s	1170 m		
1179 s			
1220 s			
	1239 m		
1256 s	1263 m		
1341 m			
1360 m			
1385 w			
1596 vs	1595 m		
1605 sh	1605 m		

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

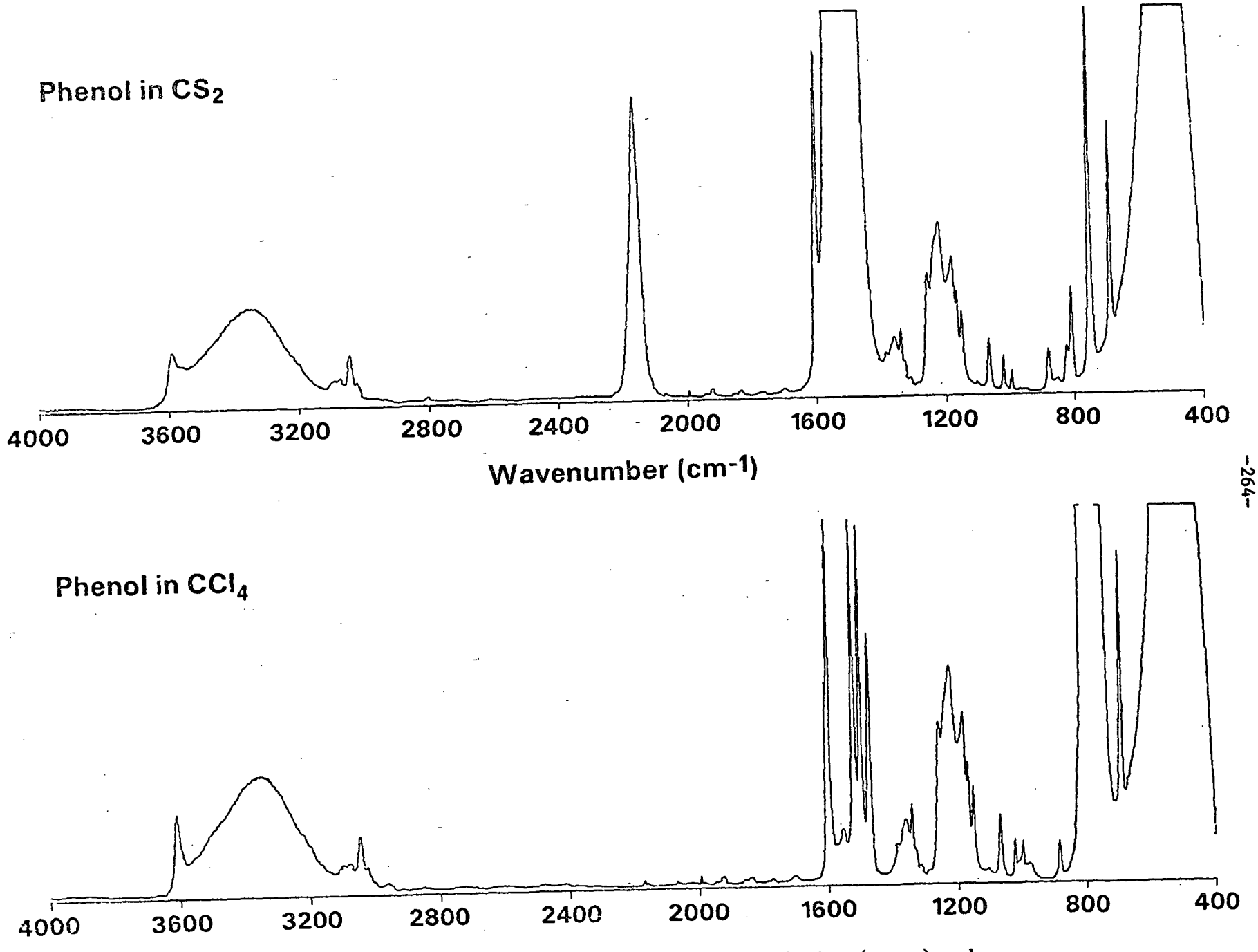


Figure 33. The infrared spectra of phenol in CS_2 solution (upper) and in CCL_4 solution (lower).

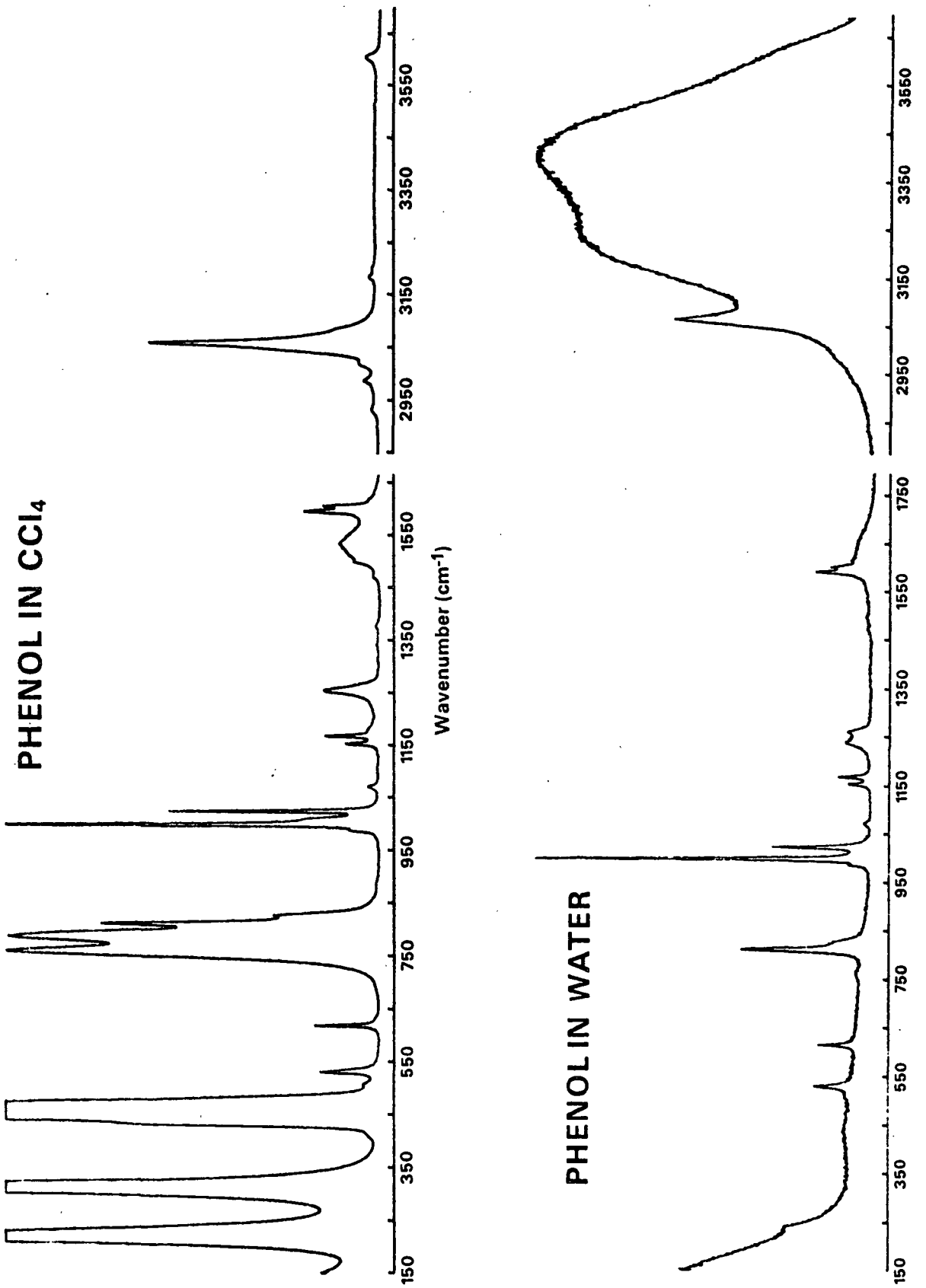


Figure 34. Raman spectra of phenol in CCl_4 solution (upper) and in aqueous solution (lower).

TABLE LV
DEPOLARIZATION RATIOS - BENZALDEHYDE(LIQUID)

Raman, cm^{-1}		Depolarization Ratio
128	m[a]	0.8
223	w	0.6
237	w	0.6
438	m	0.1
451	w	0.4
614	m	0.7
649	m	0.2
746	w	0.6
811	w	0.3
827	m	0.1
851	w	0.6
987	w	
1000	vs	0.05
1022	m	0.1
1072	w	0.5
1147	sh	0.5
1160	sh	0.4
1166	m	0.2
1202	s	0.2
1311	w	0.4
1377	sh	0.5
1390	w	0.3
1455	w	0.3
1490	w	0.4
1584	sh	0.4
1596	s	0.4
1652	w	0.4
1696	s	0.3
2693	w	0.4
2737	m	0.3
2819	m	0.3
2847	w	0.2
3007	w	0.3
3046	sh	0.3
3063	m	0.2
3101	w	0.4
3163	w	0.1
3190	w	0.2

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

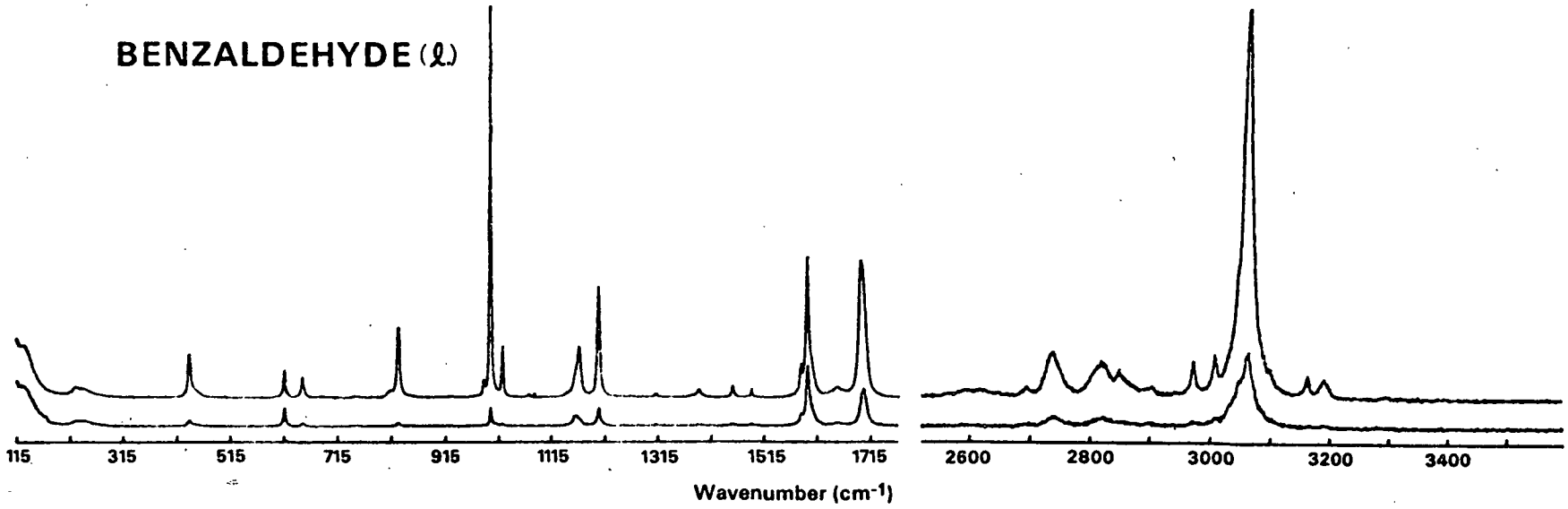


Figure 35. Raman spectra of benzaldehyde (ℓ) recorded with the analyzer parallel to the polarization of the incident light (upper) and perpendicular to the polarization of the incident light (lower).

TABLE LVI

SPECTRAL DATA - BENZALDEHYDE IN CCl_4

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	125 m[a]	1429 vw	
	406 sh	1456 m	1455 w
	ca. 527 w		1491 w
	561 vw	1522 w	
	614 m	1586 m	1584 m
650 s	649 m	1598 m	1596 ms
688 s		1654 m	1651 w
828 s	826 m	1671 vw	1668 vw
	846 sh	1708 vs	1705 ms
920 w	919 vw	2693 w	2691 w
	969 vw	2732 m	2731 w
	987 w	2814 m	2812 w
	1000 s	2847 w	2844 w
1024 w	1023 m		2893 w
1072 w	1071 w	2918 w	
1100 vw		3013 w	3008 w
	1139 w	3032 w	3032 sh
	1159 m		3049 w
1167 m	1165 m		
	1186 sh	3088 w	
1203 s	1202 ms		
	1250 vw		
	1265 vw		
1285 w	1284 w		
1310 m	1309 vw		
1337 w	1337 vw		
	1375 vw		
1388 m	1387 w		

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

TABLE LVII

SPECTRAL DATA - BENZALDEHYDE IN CS_2 (IR) OR MeOH (RAMAN)

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	226 w[a]	2689 w	
	239 w	2727 m	
	351 w	2803 m	
	440 m	2843 w	
	616 m	3012 w	3006 w
650 s	652 m	3028 w	
687 s			3051
742 s	751 vw	3064 w	3066 m
808 w	812 w	3084 w	
827 s	830 m		3165 vw
852 w	856 w		3193 vw
918 w			
	931 vw		
1002 w	1001 s		
1023 w	1025 ms		
1070 w	1073 ms		
1099 w			
	1109 w		
1165 m	1162 sh		
	1169 m		
1202 s	1205 m		
1265 w			
1283 w	1291 vw		
1309 m	1312 w		
1335 w			
1386 m	1395 w		
	1457 m		
1583 m	1585 m		
1596 m	1598 s		
1651 w	1657 w		
1669 w	1697 sh		
1706 vs	1705 ms		

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

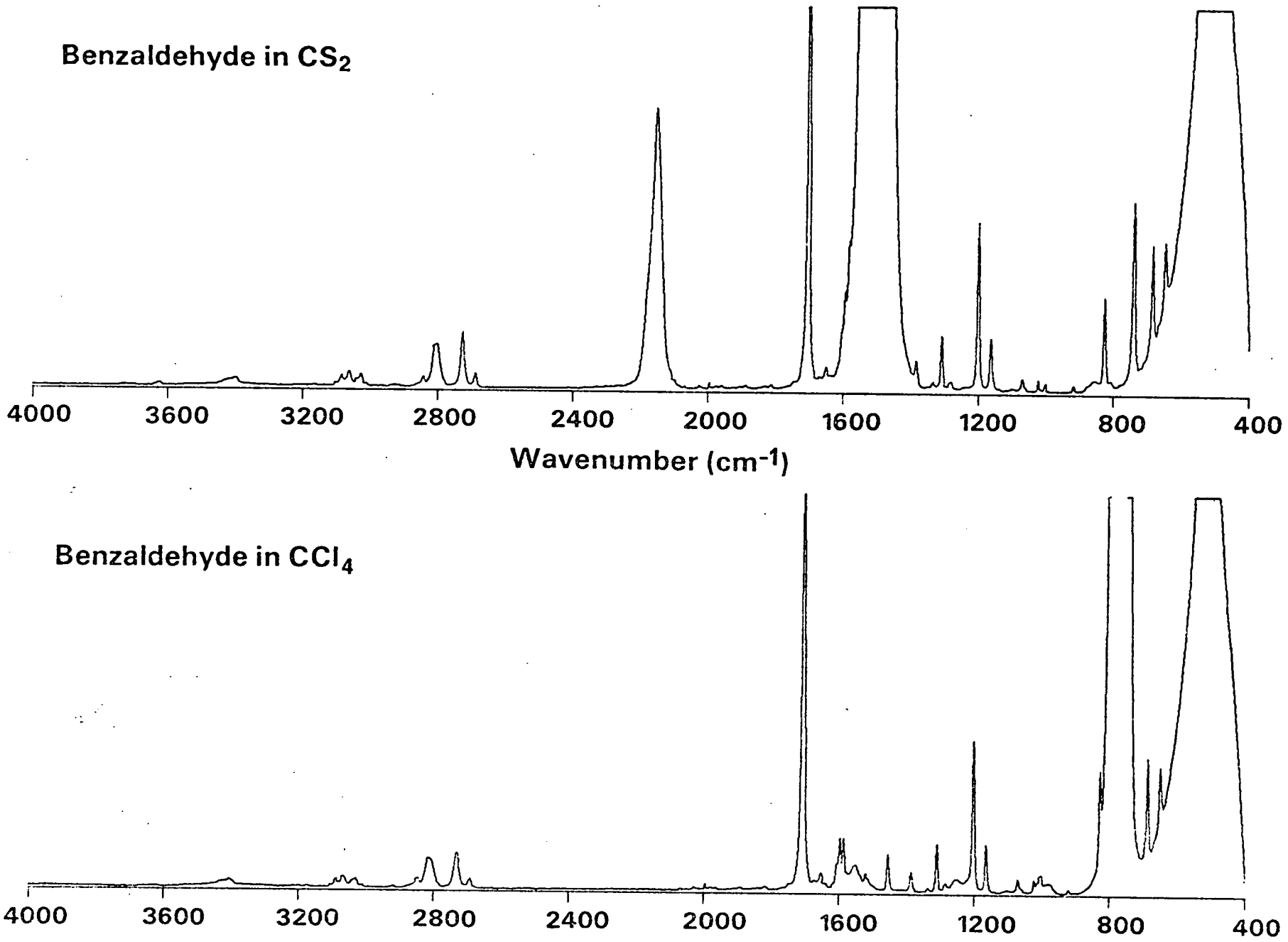


Figure 36. The infrared spectra of benzaldehyde in CS_2 solution (upper) and in CCl_4 solution (lower).

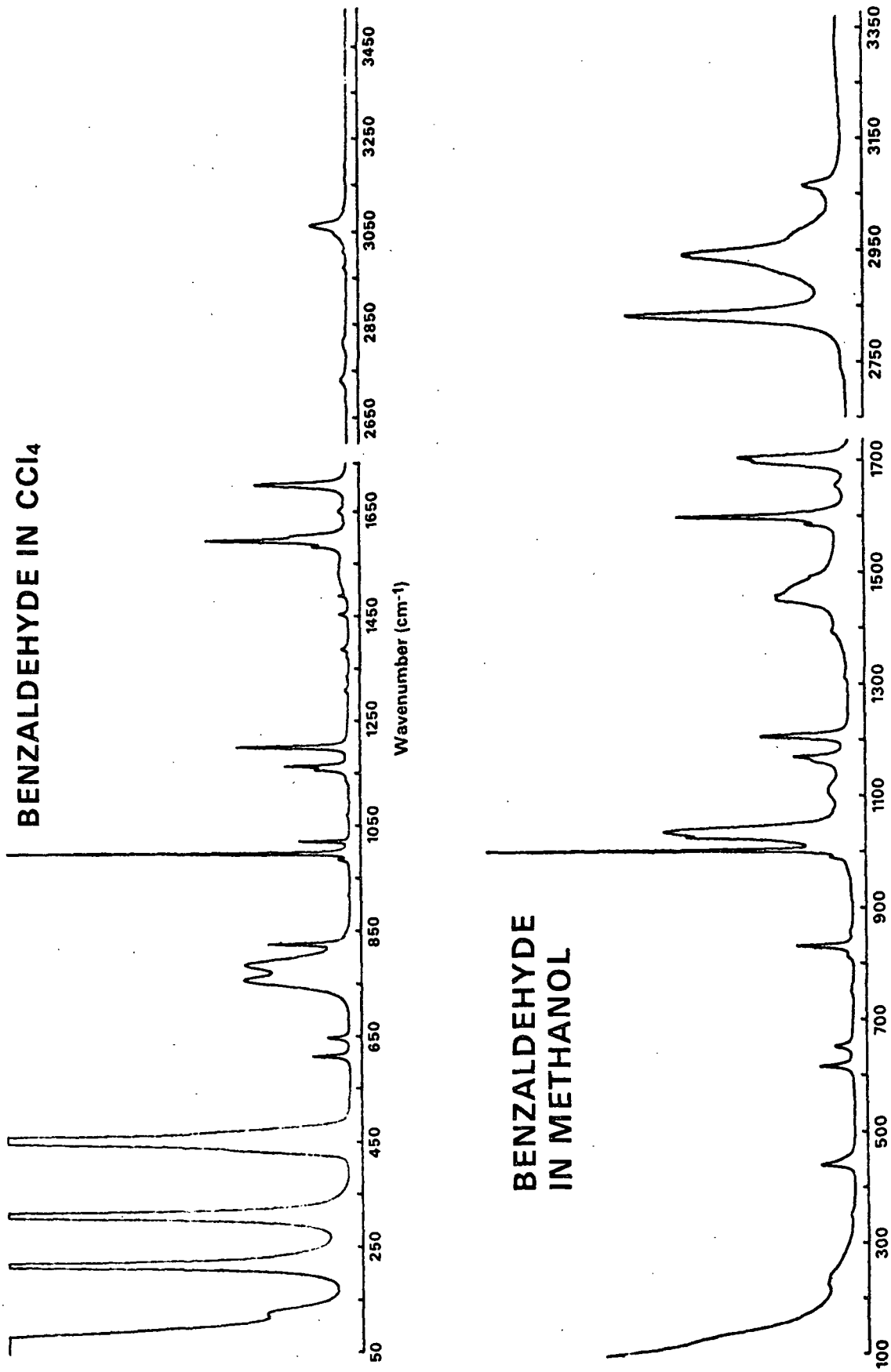


Figure 37. The Raman spectra of benzaldehyde in CCl_4 solution (upper) and in MeOH solution (lower).

TABLE LVIII

DEPOLARIZATION RATIOS - ANISOLE(LIQUID)

Raman, cm^{-1}	Depolarization Ratio
214 m[a]	0.7
266 mw	0.4
416 vw	0.6
443 s	0.2
513 w	0.6
553 w	0.6
614 s	0.6
695 vw	0.7
757 w	0.6
784 vs	0.06
820 w	0.6
885 vw	0.6
975 m	0.3
995 vvs	0.03
1021 s	0.06
1039 s	0.1
1078 w	0.5
1112 vw	0.6
1153 m	0.6
1172 s	0.3
1181 s	0.2
1228 vw	0.2
1247 s	0.1
1291 m	0.2
1302 m	0.1
1325 w	0.4
1336 w	0.4
1383 w	0.4
1441 m	0.6
1455 m	0.6
1468 w	0.6
1497 w	0.6
1548 w	0.6
1587 s	0.6
1600 s	0.6
2836 s	0.03
2926 w	0.2
2924 m	0.1
2945 m	0.1
2956 s	0.4
3004 m	0.5
3037 sh	0.4
3055 s	0.3
3069 s	0.2

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

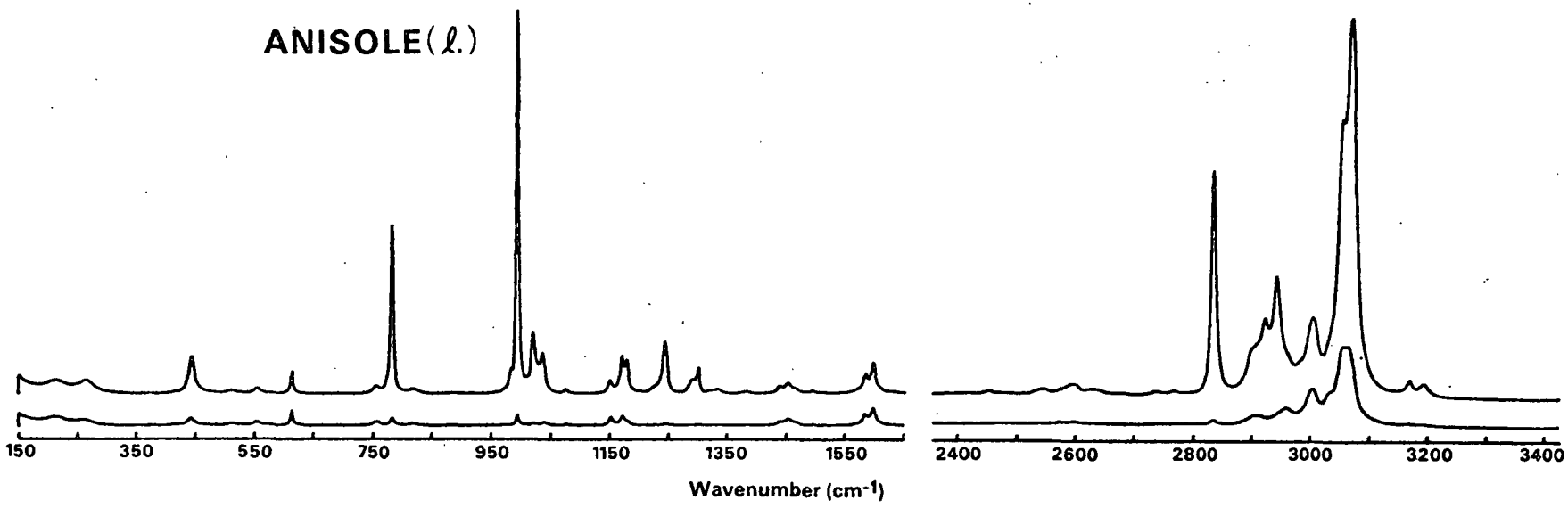


Figure 38. The Raman spectra of anisole (ℓ) recorded with the analyzer parallel (upper) or perpendicular (lower) to the polarization of the incident light.

TABLE LIX

SPECTRAL DATA - ANISOLE IN CCl_4

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	262 sh[a]	2836 m	2831 m
	416 sh		2895 w
	510 w	2907 w	2909 w
	555 w	2924 w	2920 w
	616 m	2944 m	2938 m
691 s	694 vw	2955 m	
	784 s	3003 m	2999 m
	814 sh	3034 w	3035 sh
881 m	881 w		3054 m
	958 vw	3064 w	3069 m
	975 sh	3095 w	
	985 m		3168 w
996 w	996 s		3191 vw
1022 w	1023 m		
1045 s	1041 m		
1077 m	1078 w		
1108 vw	1108 vw		
1153 w	1153 m		
1172 m	1172 m		
1182 m	1182 m		
	1228 w		
1248 vs	1248 m		
1289 m	1291 m		
1303 m	1303 m		
	1322 w		
1336 w	1336 w		
	1368 w		
	1381 vw		
1441 m	1441 m		
1454 m	1456 m		
1468 m	1467 m		
1498 s	1498 w		
1570 w			
1589 m	1588 m		
1602 s	1601 m		
	1632 sh		

[a]Strong(s), medium(m), weak (w), shoulder(sh), very(v).

TABLE LX

SPECTRAL DATA - ANISOLE IN CS_2 (IR) OR MeOH (RAMAN)

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	209 w[a]	2831 m	
	264 w	2903 w	
	419 vw	2920 w	
	444 m	2949 m	
	512 w		
	555 w	2998 m	
	615 m	3031 w	
690 s			3054 m
752 s	759 m	3062 w	3069 m
784 m	785 ms	3092 w	
824 w	821 w		
879 m			
995 w	996 s		
1022 w			
1043 s			
1076 m	1079 w		
1106 vw	1108 m		
1152 w	1155 m		
1171 m	1174 m		
1180 m	1181 m		
1200 sh			
	1229 sh		
1246 vs	1248 m		
1287 w	1295 m		
1302 m	1303 m		
	1324 w		
1334 w	1338 w		
1587 m	1588 m		
1600 s	1601 m		

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

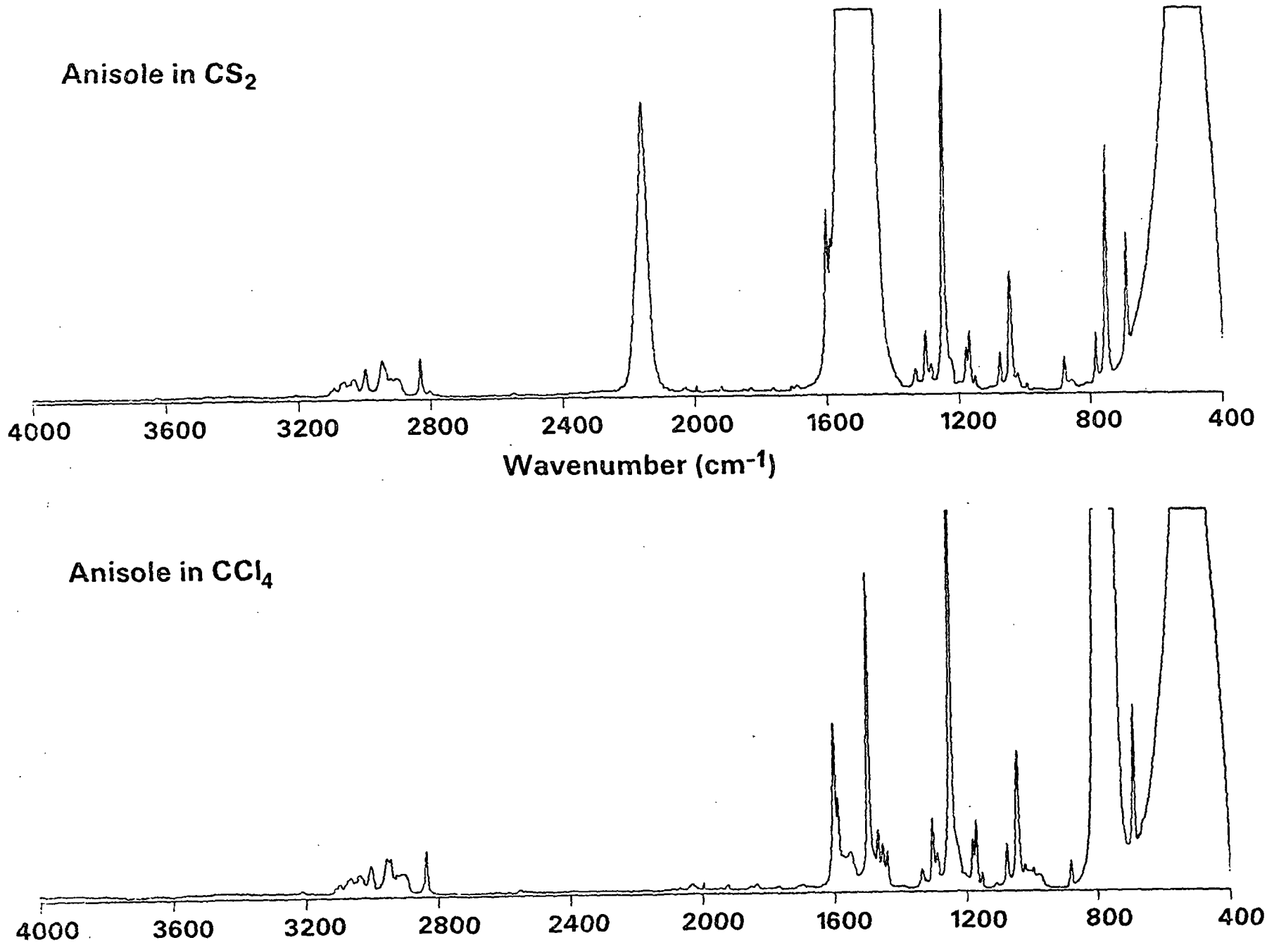


Figure 39. The infrared spectra of anisole in CS_2 solution (upper) and in CCl_4 solution (lower).

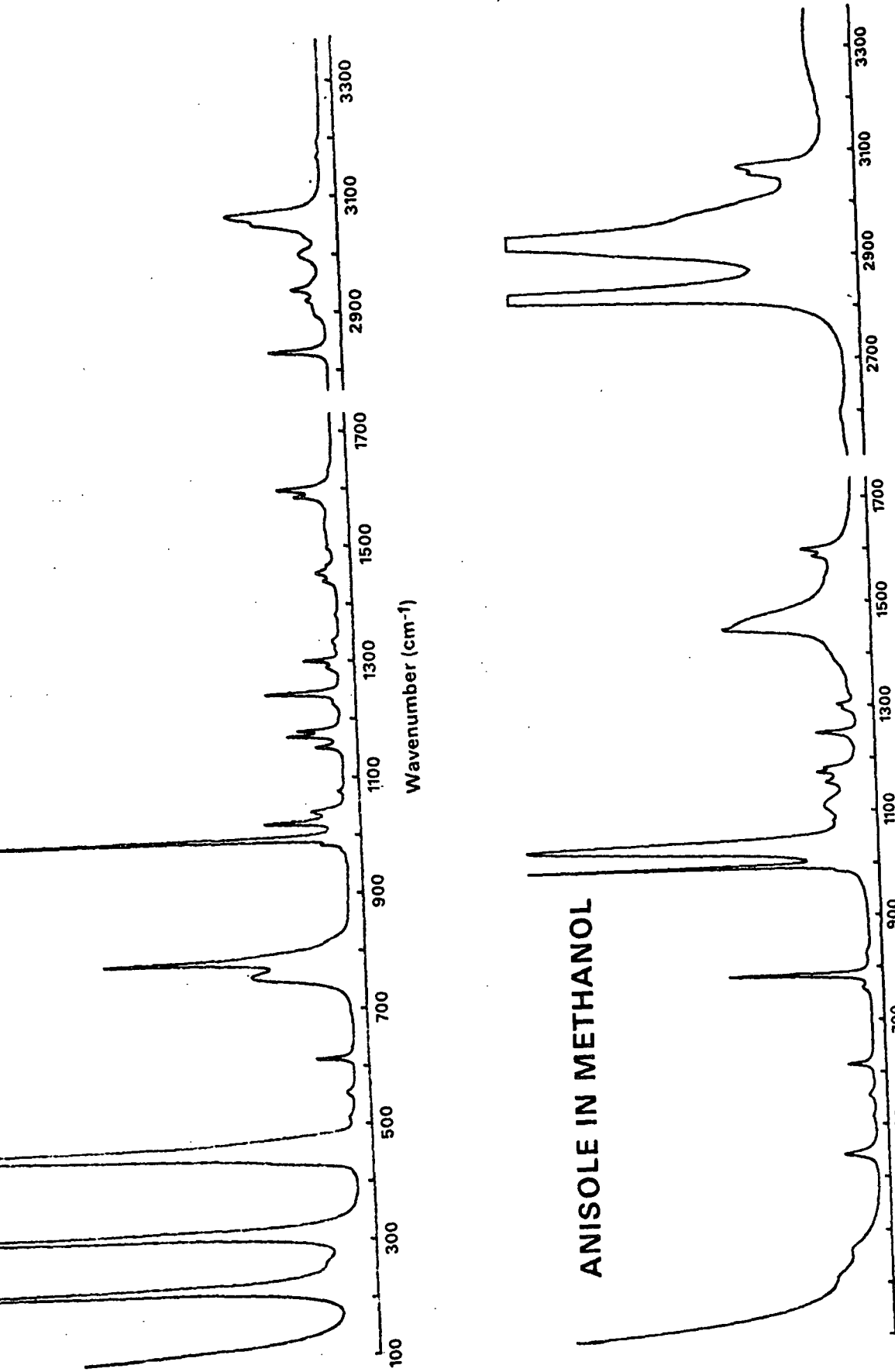


Figure 40. The Raman spectra of anisole in CCl_4 solution (upper) and in MeOH solution (lower).

TABLE LXI

DEPOLARIZATION RATIOS - 4-HYDROXYBENZALDEHYDE

Raman, cm^{-1}		Depolarization Ratio
408	m[a]	0.8
602	w	0.8
641	m	0.8
858	m	0.5
1159	s	0.4
1216	m	0.6
1282	m	0.7
1399	w	0.8
1454	w	0.8
1580	s	0.6
1597	s	0.6
1670	s	0.6

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

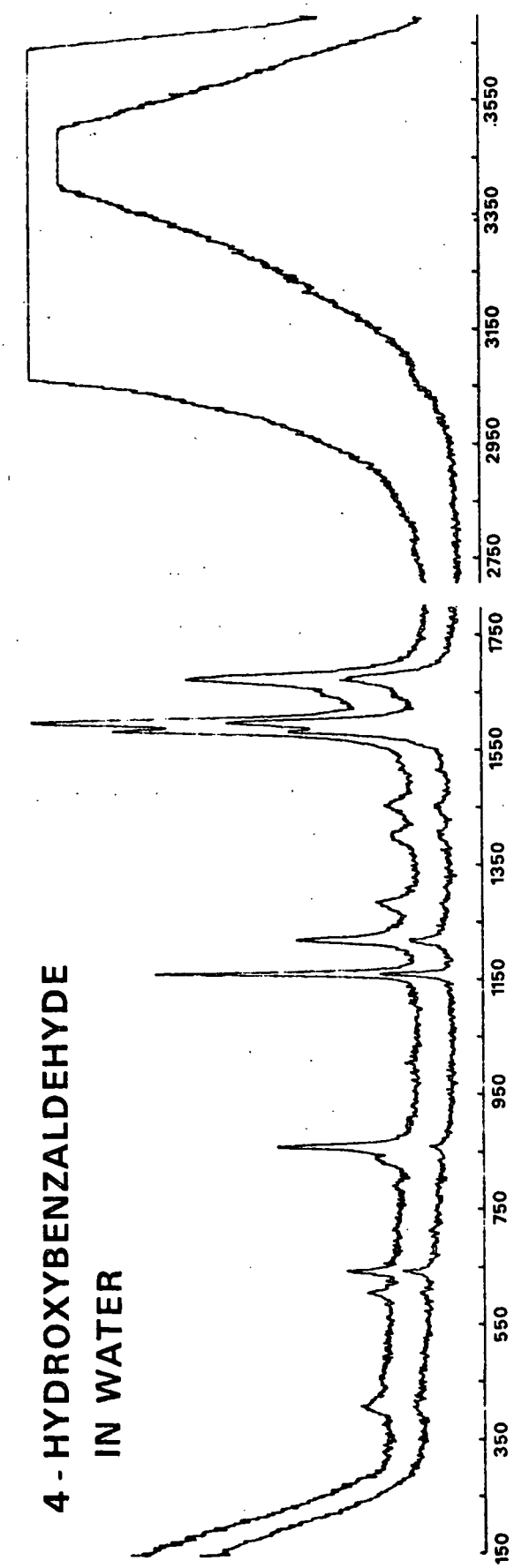


Figure 41. The Raman spectra of 4-hydroxybenzaldehyde in an aqueous solution measured with the analyzer parallel (upper) or perpendicular (lower) to the polarization of the incident radiation.

TABLE LXII

RAMAN DATA - 4-HYDROXYBENZALDEHYDE IN MeOH AND H_2O

MeOH, cm^{-1}	H_2O, cm^{-1}	MeOH, cm^{-1}	H_2O, cm^{-1}
59 sh[a]			1444 w
84 sh		(1451)	1457 w
91 sh		1519 w	
106 sh		1586 s	1588 s
123 sh		1604 vs	1603 vs
201 sh		1649 w	1654 w
325 w	330 w	1679 s	1679 s
402 m	409 m	3018 sh	
448 w		3036 vw	
464 w	464 m	3052 vw	
	602 w	3069 w	
605 m	607 m	3300 lump	
622 w			
642 m	644 m		
717 w			
788 w	794 w		
836 m	838 w		
860 m	863 m		
(1008)			
(1024)			
1157 s	1163 s		
1194 sh			
1218 m	1221 m		
1243 w			
1269 w			
1291 m	1287 m		
1399 w	1402 w		
	1409 w		

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

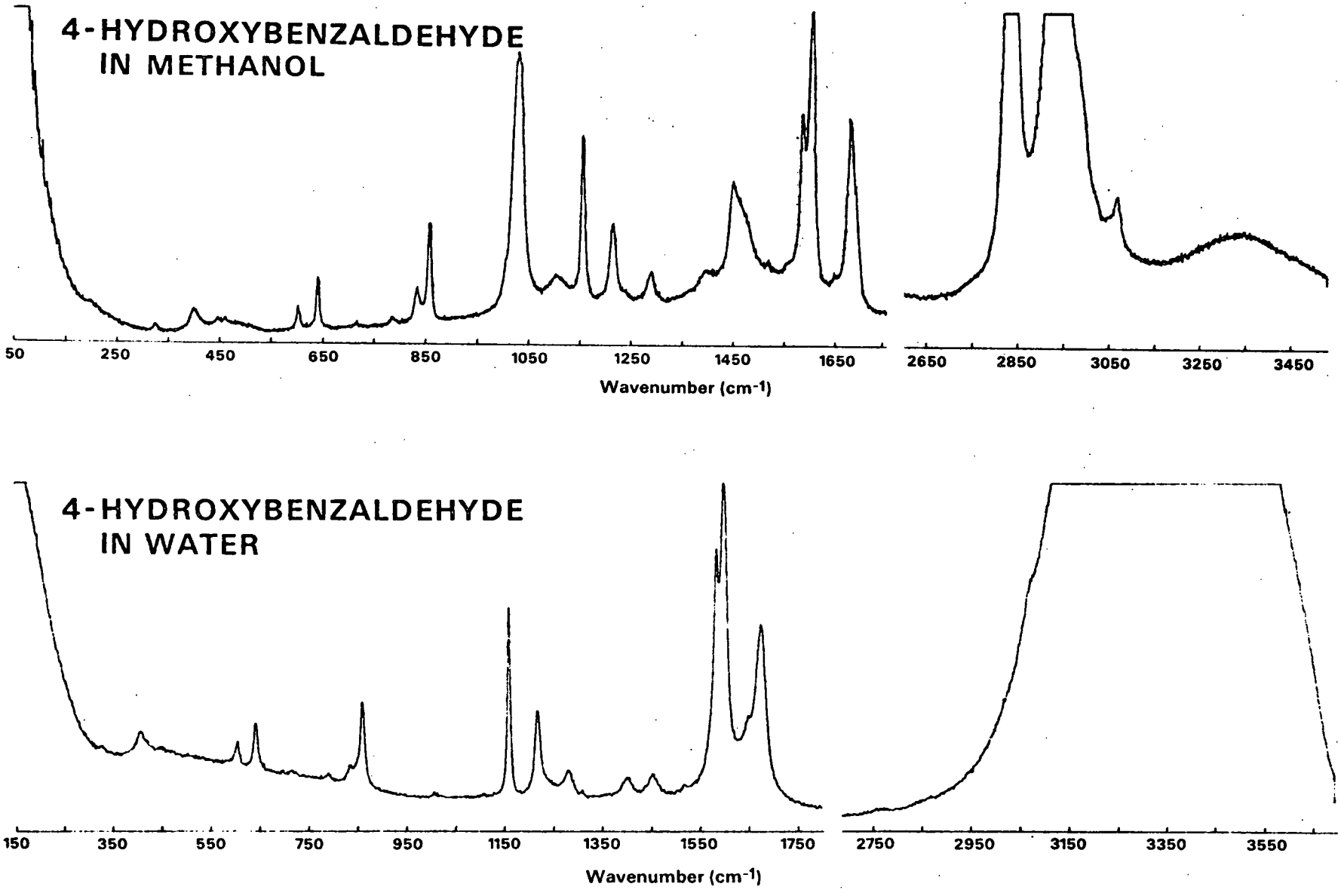


Figure 42. The Raman spectra of 4-hydroxybenzaldehyde in MeOH solution (upper) and in aqueous solution (lower).

TABLE LXIII

DEPOLARIZATION RATIOS - GUAIACOL

Raman, cm^{-1}	Depolarization Ratio	Raman, cm^{-1}	Depolarization Ratio
188 m[a]	0.6	1292 sh	0.1
236 m	0.5	1301 m	0.09
310 m	0.6	1357 m	0.1
346 m	0.2	1443 m	0.5
456 m	0.6	1454 m	0.5
502 m	0.3	1461 m	0.5
534 m	0.4	1502 m	0.2
570 m	0.4	1596 s	0.6
583 m	0.5	1609 m	0.6
727 m	0.3	1681 w	0.3
759 vs	0.06	2840 m	0.03
834 m	0.09	2910 w	0.1
913 w	0.2	2931 w	0.06
962 w	0.4	2944 w	0.09
1027 s	0.06	2965 sh	0.4
1038 s	0.06	3009 w	0.4
1109 w	0.4	3023 w	0.5
1134 sh	0.2	3053 sh	0.3
1155 s	0.3	3070 m	0.2
1172 m	0.2	3514 w	0.2
1206 m	0.3		
1223 w	0.2		
1263 s	0.06		

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

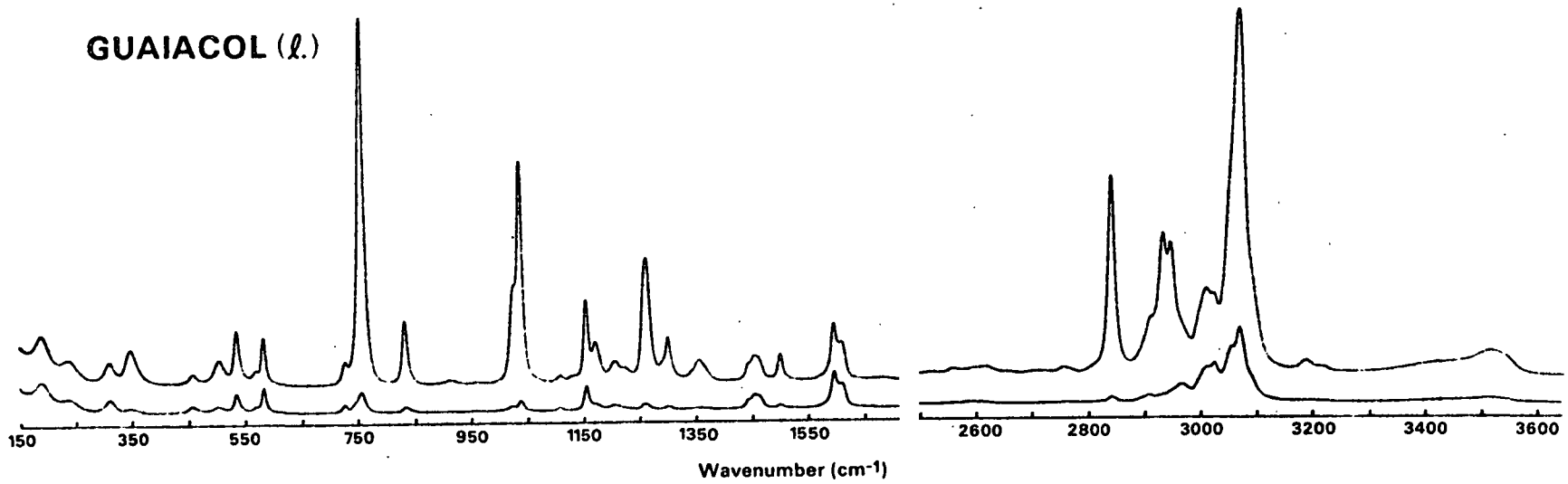


Figure 43. The Raman spectra of guaiacol (ℓ) measured with the analyzer parallel (upper) or perpendicular (lower) to the polarization of the incident light.

TABLE LXIV

SPECTRAL DATA - GUAIACOL IN CCl_4

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	189 m[a]	1405 w	
	343 m	1444 m	1443 m
	501 w	1454 m	1453 m
	534 m	1463 m	1462 m
	568 w	1471 m	
	583 m		1485 sh
	726 m	1502 vs	1502 m
	758 s	1523 m	
	834 m	1580 w	
913 w	916 w	1599 m	1599 m
980		1617 w	1609 m
1027 m	1027 ms	1996	
1042 m	1039 ms	2843 m	2841 m
1110 m	1110 w	2911 w	2909 m
	1131 w	2935 w	2931 m
1155 w	1155 m	2949 m	2946 m
1175 m	1175 m	2961 m	2964 sh
1208 m	1207 m	3007 w	3005 sh
1225 s	1224 w		3024 m
1260 vs	1260 ms		3039 m
	1290 w	3058 w	3055 sh
1303 w	1302 m		3070 m
	1361 m		3091 sh
1367 m	1366 m		3190 w
			3220 w
		3556 m	3549 w

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

TABLE LXV

SPECTRAL DATA - GUAIACOL IN CS_2 (IR) OR MeOH (RAMAN)

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	237 sh[a]	1404 m	
	310 w		1451 m
	358 m		1503 m
	460 w	1598 m	1599 m
	505 m	1616 m	1610 sh
	542 m	1996 w	
	559 sh	2839 m	
	570 w	2905 w	
	586 m	2929 m	
	729 sh	2944 w	
741 s		2957 m	
757 m	758 s	3003 w	
786 m		3054 w	3055 sh
836 w	838 m		3070 m
910 w			3191 w
	ca. 920 w		3327 w
	ca. 962 w		
1026 m			
1040 m			
1109 m	1111 m		
1154 w	1158 m		
1176 m	1177 m		
1206 m	1215 w		
1223 s			
	1251 sh		
1259 s	1266 m		
	1279 sh		
	1295 sh		
1301 w	1305 sh		
	1311 m		
1365 m	1360 sh		

[a]Strong(s), medium(m), weak(w), shoulder(sh), very(v).

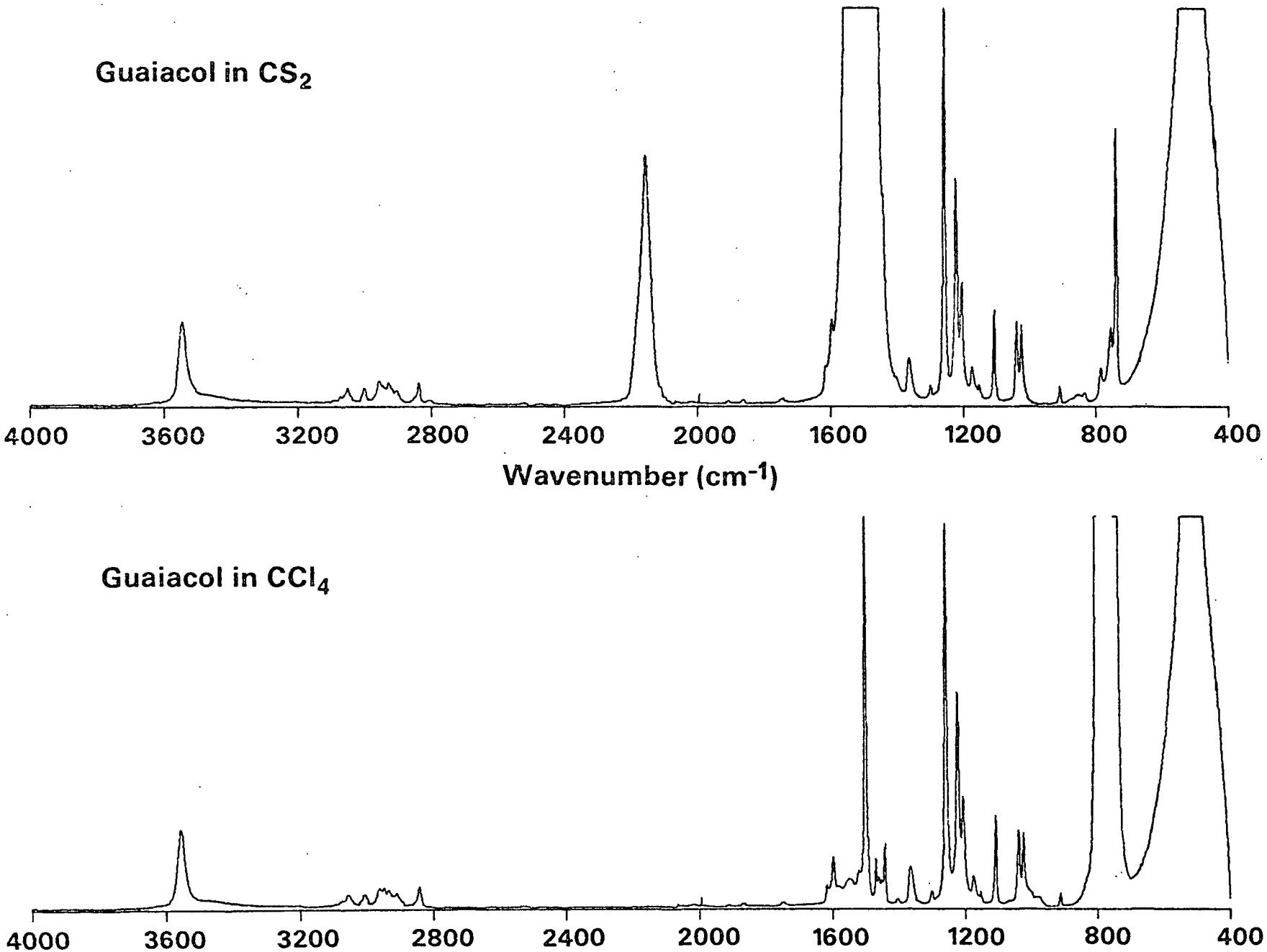


Figure 44. The infrared spectra of guaiacol in CS_2 solution (upper) and in CCl_4 solution (lower).

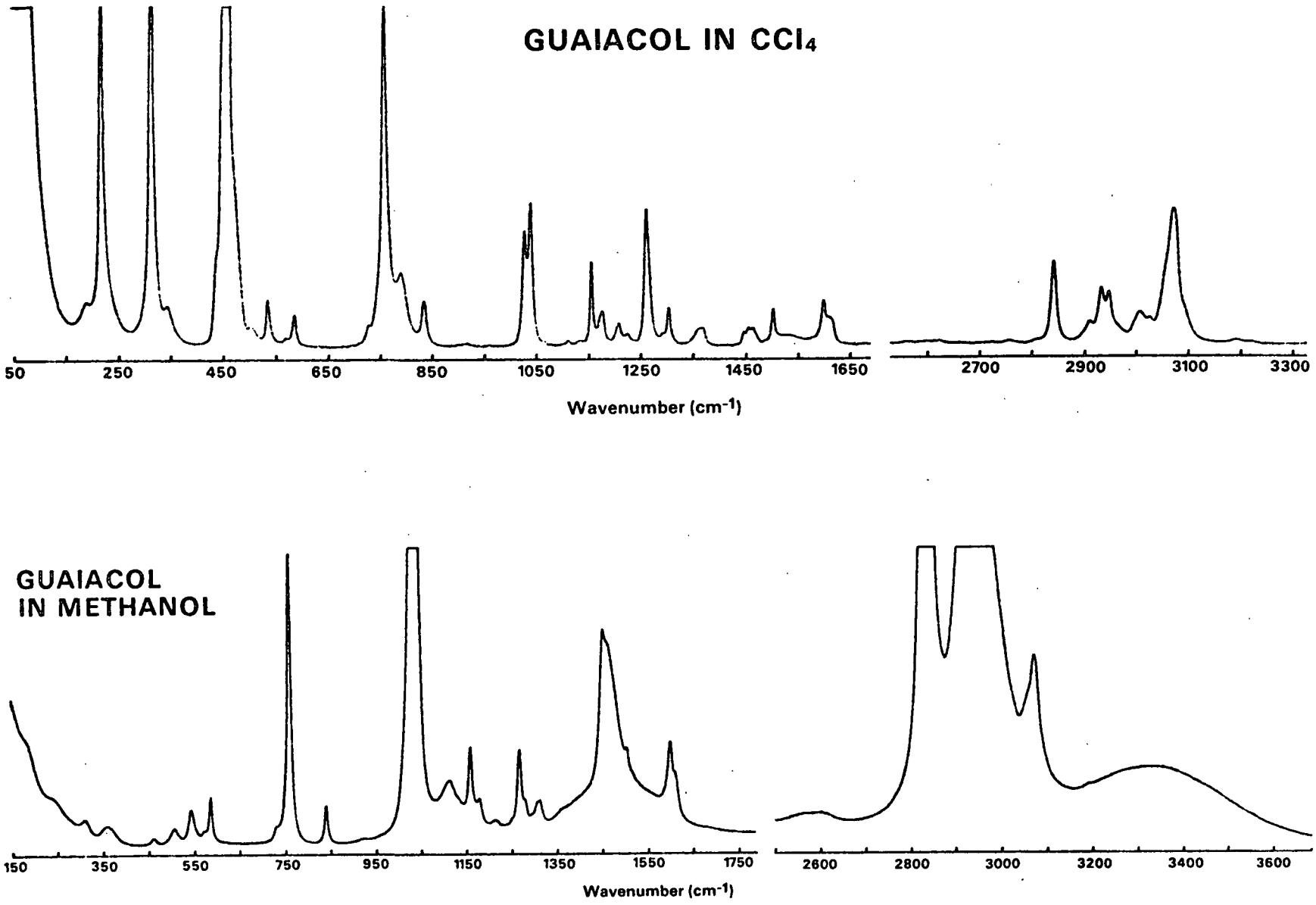


Figure 45. The Raman spectra of guaiacol in CCl_4 solution (upper) and in MeOH solution.

TABLE LXVI

DEPOLARIZATION RATIOS - m-ANISALDEHYDE

Raman, cm^{-1}	Depolarization Ratio	Raman, cm^{-1}	Depolarization Ratio
167 m[a]		1253 m	0.2
209 m		1262 s	0.2
230 m		1285 m	0.3
279 m	0.7	1291 sh	0.3
379 m	0.3	1324 m	0.3
422 w	0.8	1384 w	0.7
447 m	0.3	1457 m	0.9
456 m	0.3	1484 m	0.8
470 sh	0.5	1589 s	0.8
554 m		1599 s	1
565 m		1606 s	1
648 m	0.4	1682 s	0.4
661 w	0.3	1699 s	0.5
684 w	0.5	2001 w	0.4
738 m	0.08	2806 w	0.2
745 m	0.08	2835 m	0.07
770 m	0.2	2869 vw	0.2
788 w	0.8	2919 vw	0.1
871 w	0.9	2941 w	0.08
887 w	0.9	2963 vw	0.3
901 w	0.9	3012 w	0.3
917 w	0.9	3060 sh	0.2
930 w	0.8	3070 m	0.2
952 w	0.7	3181 vw	0.2
983 m	0.1		
994 vs	0.06		
1002 w			
1037 m	0.4		
1043 m	0.4		
1079 m	0.6		
1087 w	0.5		
1149 s	0.6		
1164 m	0.9		
1191 m	0.4		

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

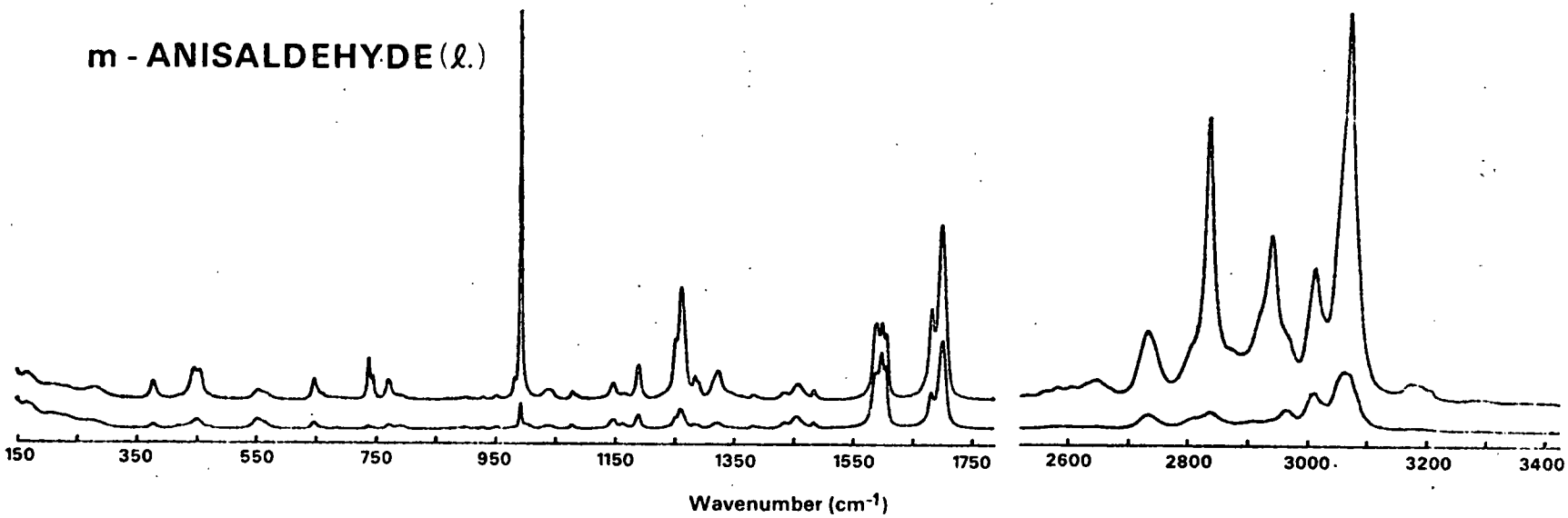


Figure 46. The Raman spectra of m-anisaldehyde (ℓ) measured with the analyzer parallel (upper) or perpendicular (lower) to the polarization of the incident radiation.

TABLE LXVII

SPECTRAL DATA - ANISALDEHYDE IN CCl_4

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	167 w[a]	1588 s	1589 s
	378 m	1598 s	1598 s
426 w			1606 m
	554 w	1686 s	1683 ms
647 s	648 m	1708	1706 s
671 m		1996	
682 s		2727 m	2725 w
	738 m	2810 m	2819 w
852 w		2819 m	
869 m		2839 m	2835 m
891 w		2876 w	
902 w		2880 w	
917 vw		2921 m	2920 vw
931 w	930 w	2926 m	
950 w	953 w	2936 m	
981 w	983 m	2943 m	2941 w
994 m	994 vs	2961 m	2959 vw
1002 w		3008 w	3008
1042 m	1040 w		3012 w
1050 m	1049 w		3053 w
1079 w	1079 m	3074 w	3073 m
	1087 w		3185 vw
1148 s	1147 m		
1164 s	1163 w		
1193 m	1192 m		
1228 w			
1253 m	1253 m		
1262 vs	1261 s		
1285 s	1285 m		
1291 m	1291 w		
1323 m	1323 m		
1336 w			
1345 w	1344 w		
	1362 w		
1382 m	1381 w		
1390 m			
1409 w			
1415 w			
1434 m	1433 w		
1459 m	1455 m		
1466 s	1464 w		
1486 s	1485 m		

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

TABLE LXVIII

SPECTRAL DATA - m-ANISALDEHYDE IN CS_2 (IR) OR MeOH (RAMAN)

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	273 w[a]	1586 s	1591 s
	378 m	1597 s	1599 s
	424 w	1685 m	1683 s
	446 m	1707 vs	1703 s
	455 m	1996	
	554 w	2721 m	
647 m	647 m	2804 m	
	662 w	2834 m	(2831)
682 ms	683 w	2872 w	
738 m	738 m		(2913)
744 m	745 m	2933 m	
776 m	773 m		(2940)
786 m	789 w	2954 m	
851 w			2977 sh
868 m		3003 m	
887 w			3013 sh
901 w	901 w	3050 w	3056 sh
930 w	931 w	3062 w	3062 sh
950 w	952 w	3071 w	3072 w
	983 m		3085 sh
994 vs	994 vs		
1000 w			
1041 m			
1049 m			
1078 w	1080 m		
	1107 m		
1147 sh	1151 m		
1162 m			
1191 m	1191 m		
1226 w			
1252 m	1253 m		
1261 vs	1263 s		
1265 s			
1284 m	1287 w		
1290 m			
1322 m	1324 m		
1336 m			
1342 m			
1380 m	1385 w		
1389 m			

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

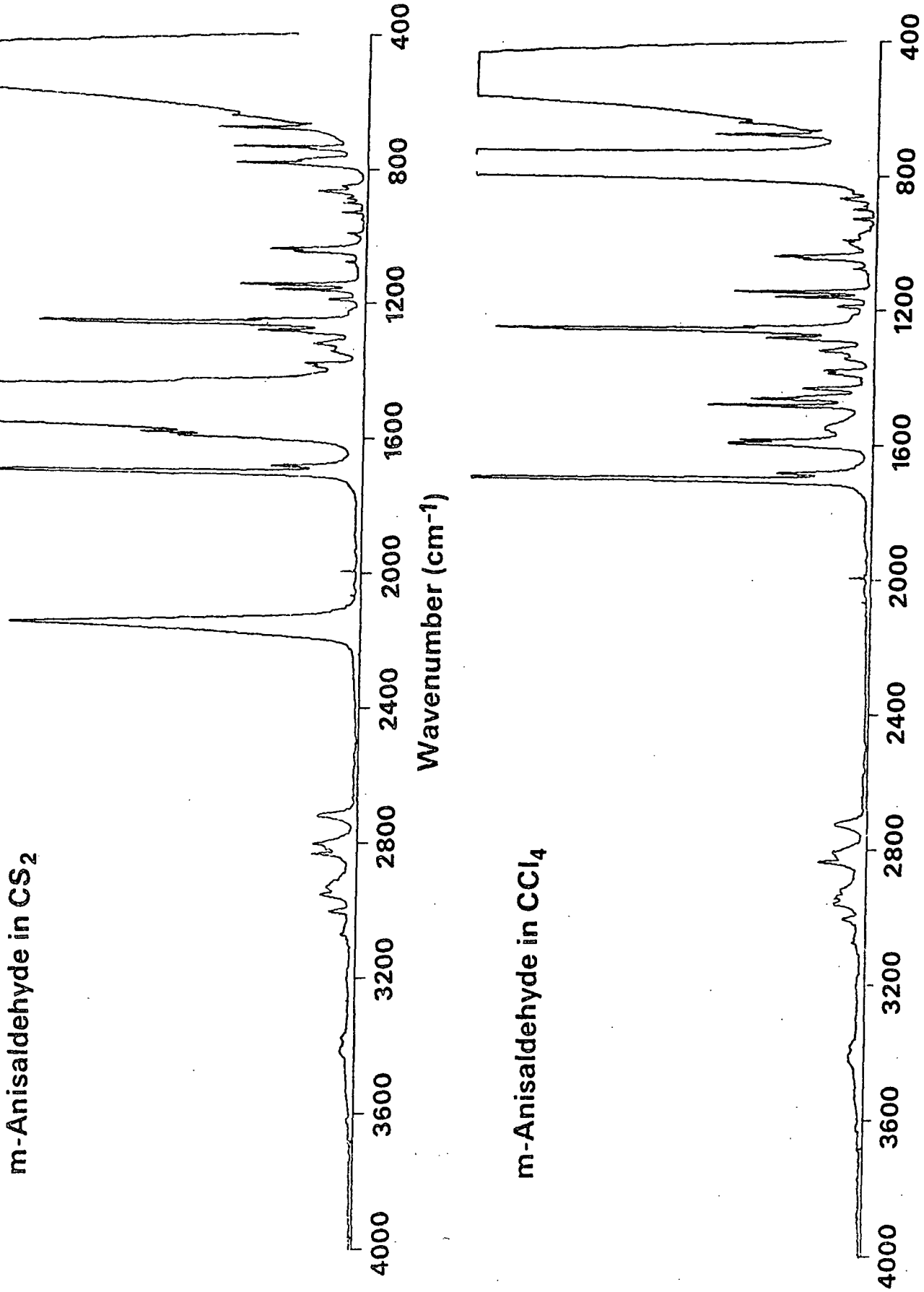


Figure 47. The infrared spectra of m-anisaldehyde in CS_2 solution (upper) and in CCl_4 solution (lower).

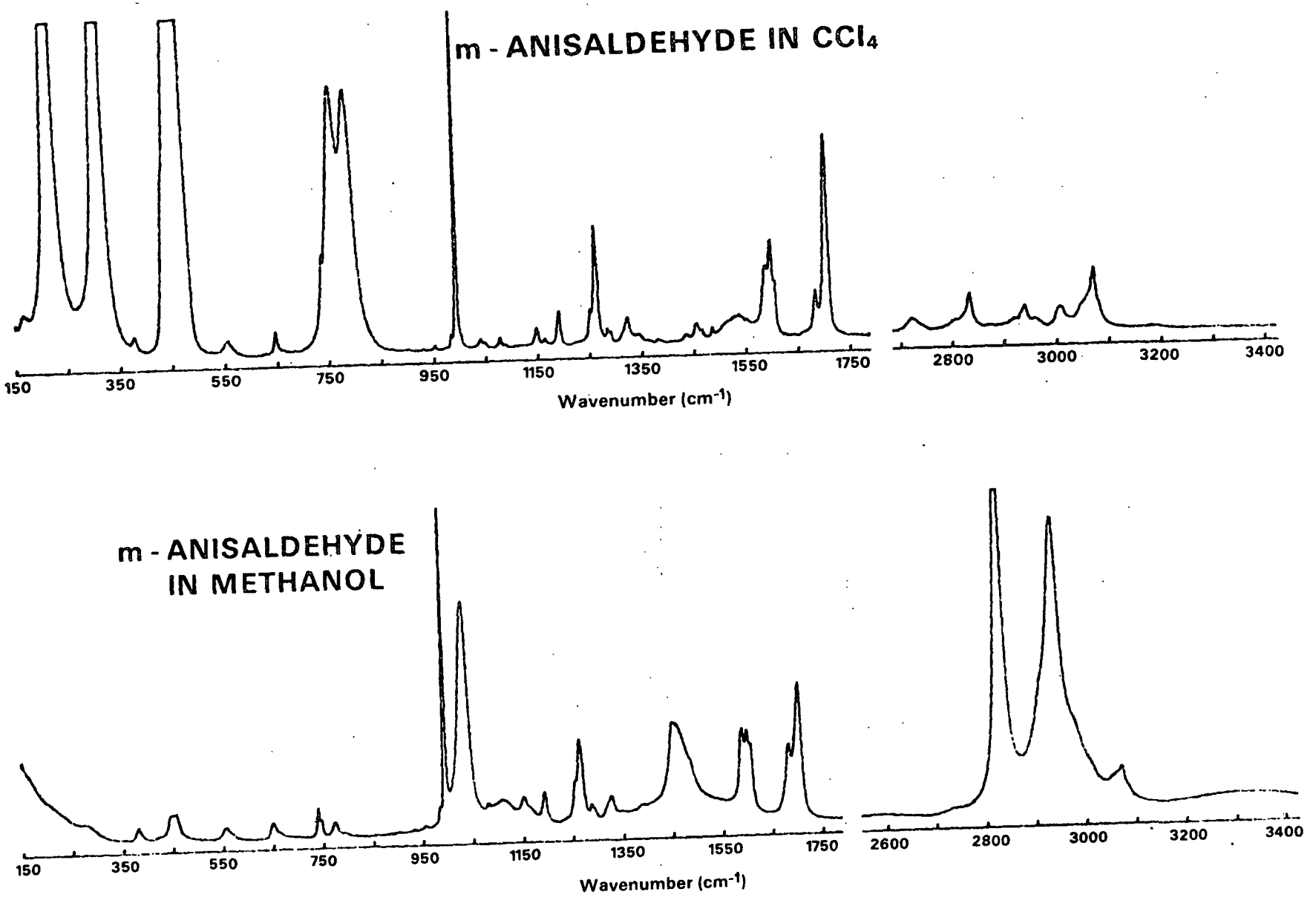


Figure 48. The Raman spectra of m-anisaldehyde in CCl_4 solution (upper) and in MeOH solution.

TABLE LXIX

DEPOLARIZATION RATIOS - VANILLIN IN H_2O OR CCl_4

Raman, cm^{-1}	Depolarization Ratio	Raman, cm^{-1}	Depolarization Ratio
148 w[a]	0.7	1499 w	
172 sh	0.7	1515 m	0.1
377 sh	0.8	1555 sh	0.3
406 sh	0.4	1599 vs	0.5
416 sh	0.2	1681 s	0.3
436 sh	0.02	1697 vs	0.3
539 m	0.6	1998 vw	0.7
550 w	0.6	2323 vw	0.7
628 s	0.4	2583 vw	
639 w	0.5	2665 vw	
929 w		2711 vw	0.7
957 m		2723 vw	
1002 w		2730 vw	
1034 m	0.4	2749 vw	
1114 w		2767 vw	
1121 m	0.3	2781 vw	
1150 m	0.4	2794 vw	0.8
1176 m	0.3	2822 vw	
1187 m	0.2	2835 vw	0.7
1209 m	0.3	2842 vw	0.7
1249 m	0.5	2856 vw	
1269 s	0.1	2874 w	0.8
1281 sh	0.2	2889 vw	
1290 sh		2903 vw	
1379 m	0.2	2923 vw	0.8
1401 m	0.3	2942 w	0.6
1437 m	0.4	2967 w	0.7
1454 m	0.4	3012 vw	0.7
1465 m	0.3	3034 vw	
		3076 w	0.6
		3198 vw	
		3535 w	0.8
		3611 vw	

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

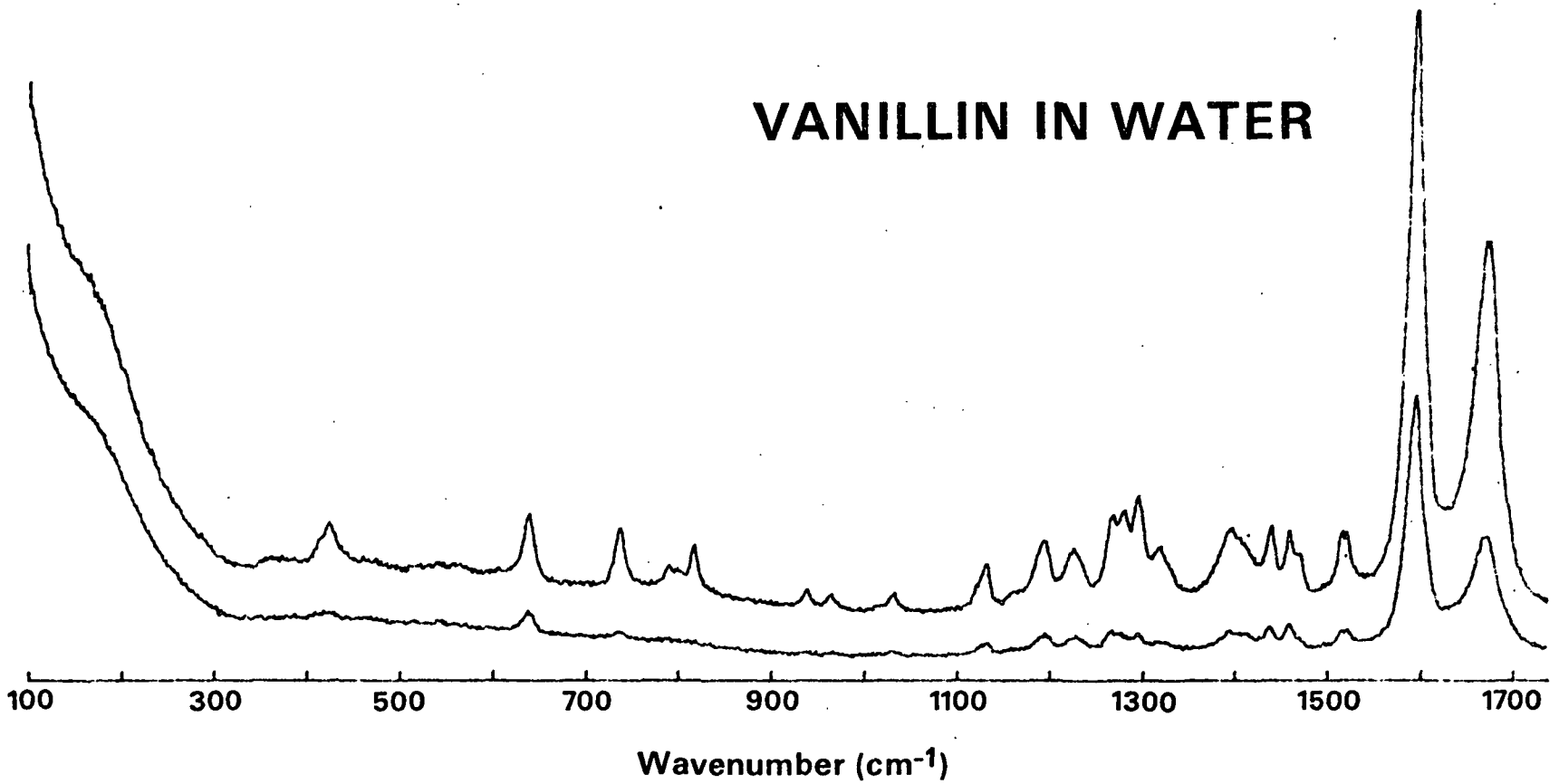


Figure 49a. The Raman spectra of vanillin in solution measured with the analyzer parallel (upper) or perpendicular (lower) to the polarization of the incident radiation.

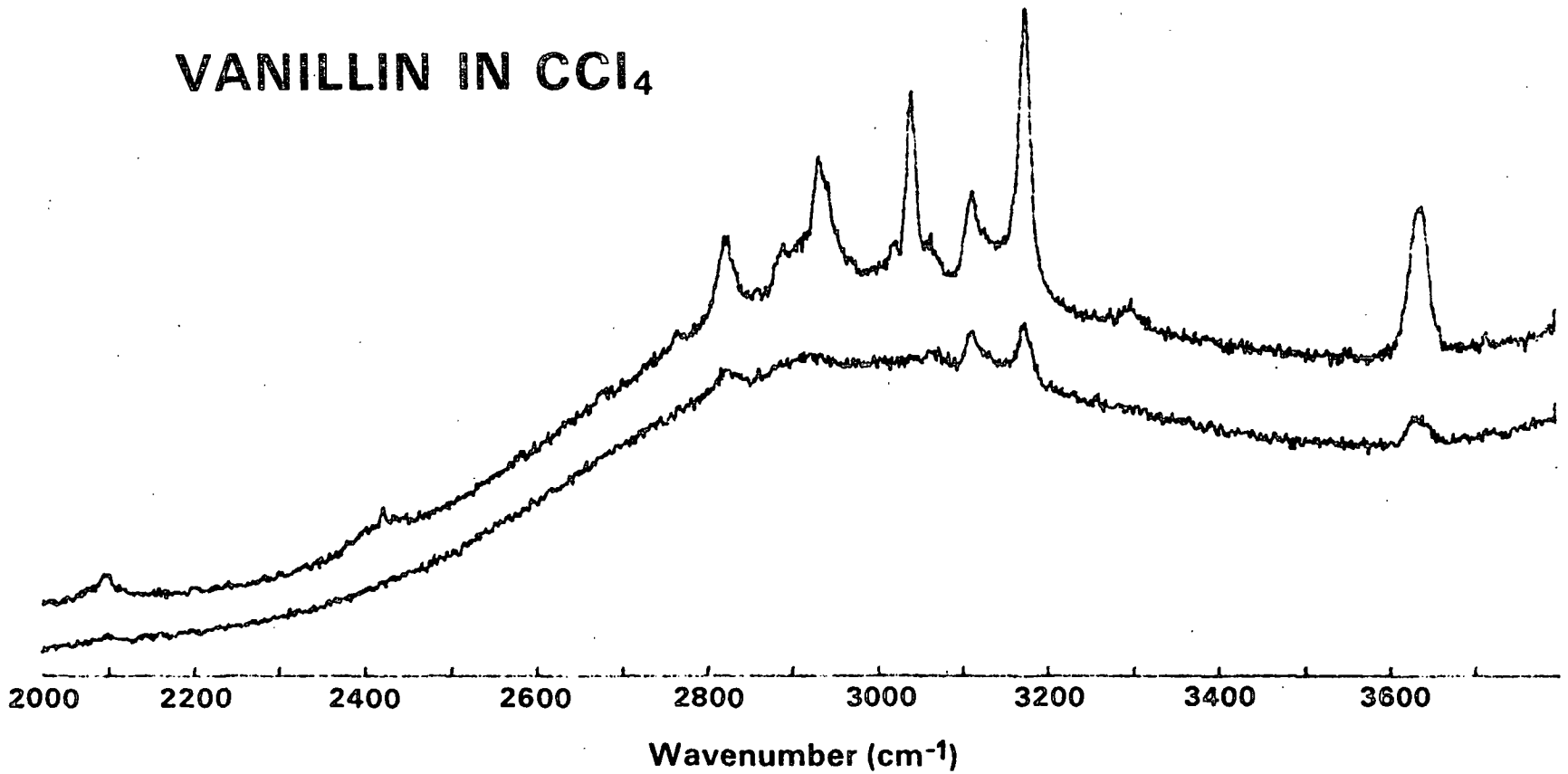


Figure 49b. The Raman spectra of vanillin in solution measured with the analyzer parallel (upper) or perpendicular (lower) to the polarization of the incident radiation.

TABLE LXX

SPECTRAL DATA - VANILLIN IN CCl_4

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	148 w[a]	1732 vw	
	172 sh	1740 w	
	377 sh	1996 m	1998 w
	406 sh	2067 w	
	416 sh		
	436 sh		
	539 m		
	550 w		
	628 s	2722 m	
	639 w	2726 w	
668 s			
872 m			
	929 w		
	957 m		
979 m		2821 m	2822 vw
1003 m	1002 w		2835 vw
1005 m			2842 vw
1034 s	1034 m		
1068 m			2874 vw
1090 w			2889 vw
1113 m	1114 w		2903 vw
1120 s	1121 m	2920 m	2923 vw
1149 s	1150 m	2940 m	2942 vw
1175 s	1176 m	2965 w	2967 vw
1186 m	1187 m		3012 w
1208 s	1209 m		3034 w
1248 s	1249 m		3076 w
1268 vs	1269 s		3198 vw
1281 s	1281 sh	3538 m	3535 vw
1291 s	1290 sh		3611 vw
1379 m	1379 m		
1401 m	1401 m		
1436 s	1437 m		
1455 m	1454 m		
1466 s	1465 m		
1509 vs	1510 s		
1550 s	1555 sh		
1599 s	1599 vs		
1682 m	1681 s		
1697 s	1697 vs		

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

TABLE LXXI

SPECTRAL DATA - VANILLIN IN CS_2 (IR) or H_2O (RAMAN)

Infrared, cm^{-1}	Raman, cm^{-1}	Infrared, cm^{-1}	Raman, cm^{-1}
	422 m[a]	1378 m	
	637 m	1399 m	1395 m
	736 m		1409 sh
	789 w		1425 w
	797 w		1438 m
817 m	815 m		1457 m
826 m			1514 m
854 m			1517 m
870 m			1594 vs
935 w	937 w		1666 sh
960 w	965 w		1670 sh
1033 m	1033 w	1681 m	
1070 w		1696 vs	
1112 m		1741 w	
1119 m		1996 m	
	1131 m	2067 w	
1148 s			
	1161 w	2718 w	
1173 m	1168 sh	2789 w	
1184 m		2801 m	
	1194 m		2847 sh
1206 m		2852 w	2853 sh
	1225 m	2926 m	
1246 m			2955 sh
1266 vs	1268 m	2961 m	
1280 s	1280 m	3010 w	
1290 sh	1294 m		3034 sh
1316 w	1317 w		
1326 w			
1336 w			

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

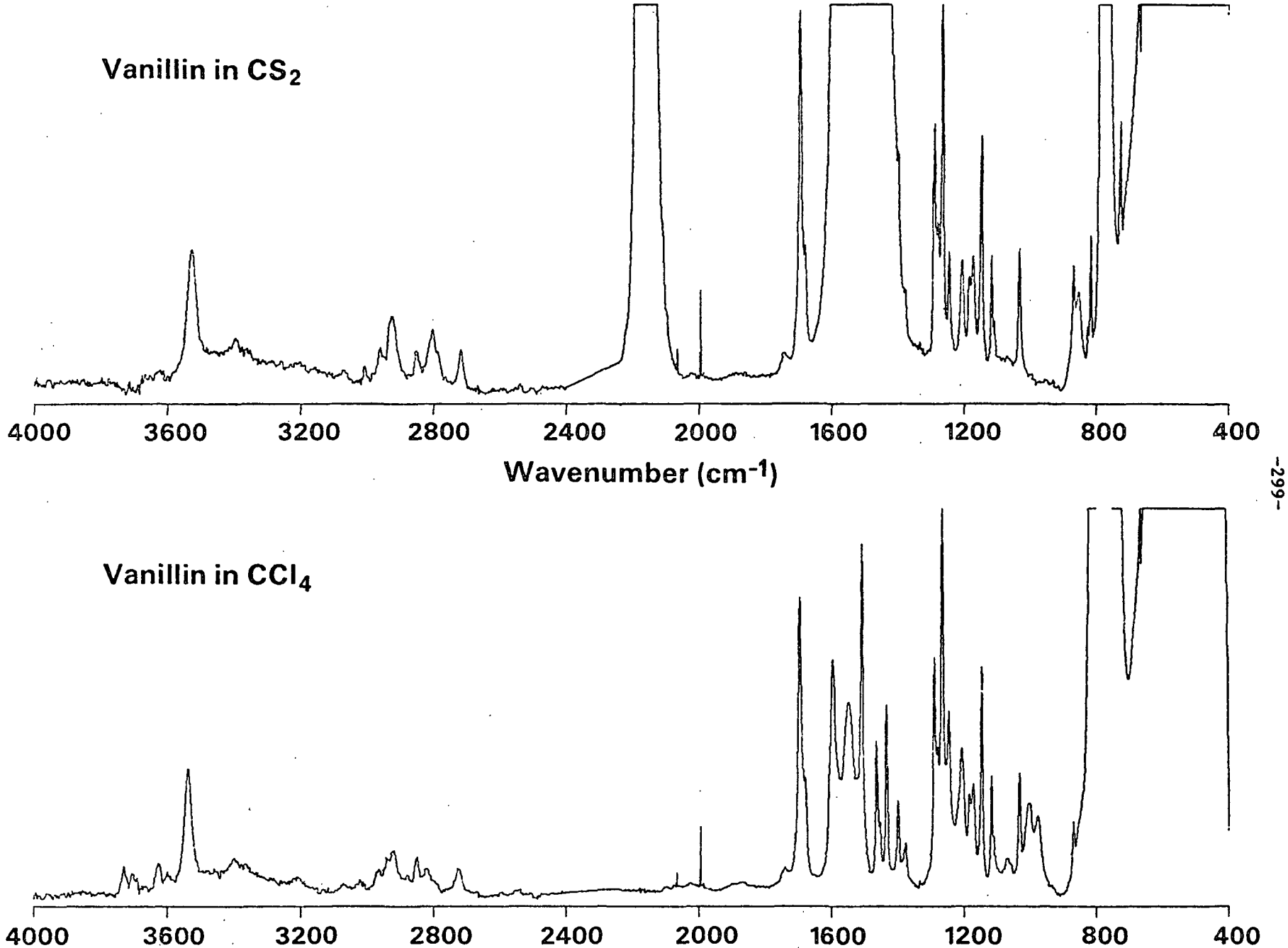


Figure 50. The infrared spectra of vanillin in CS_2 solution (upper) and CCl_4 solution (lower).

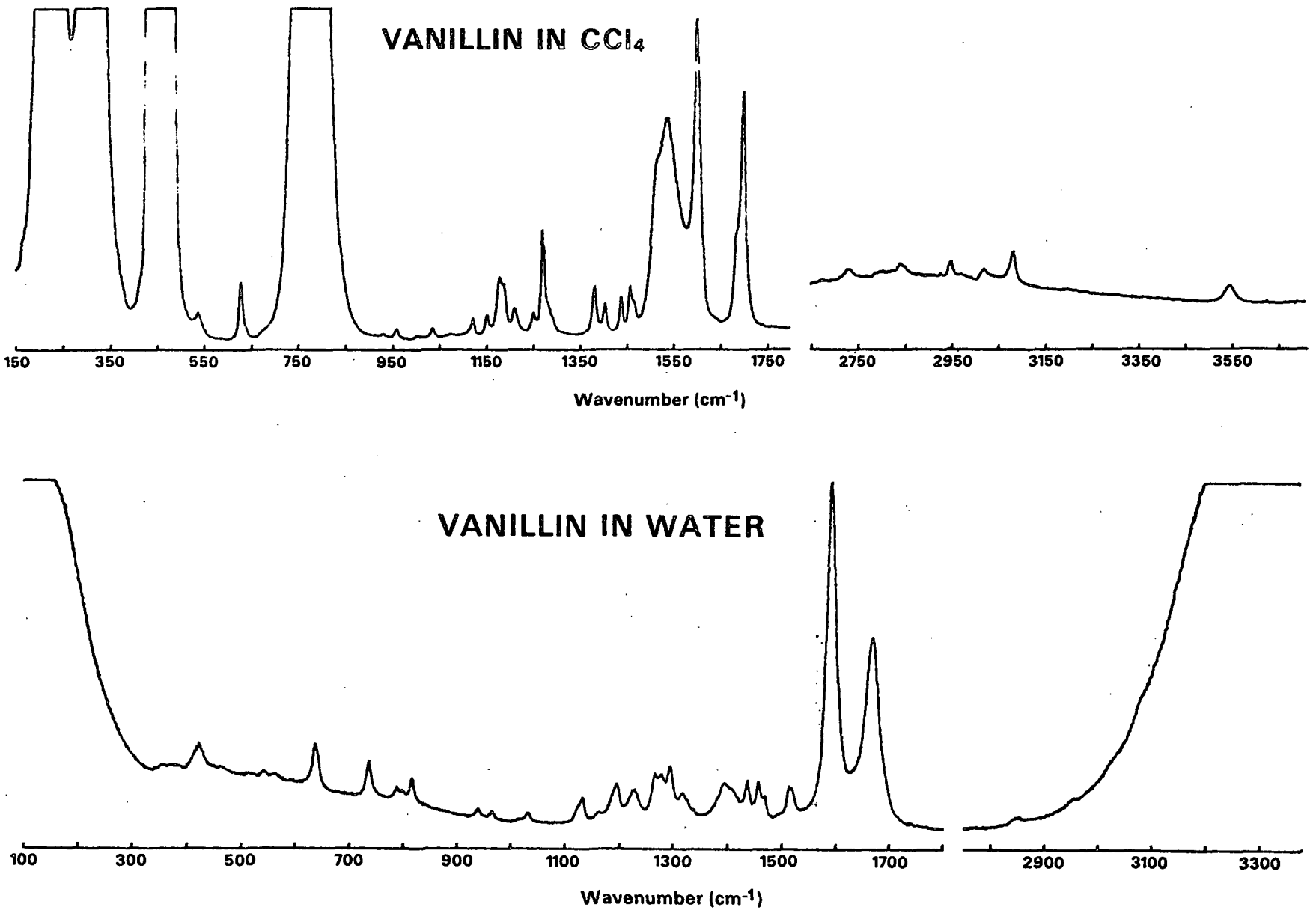


Figure 51. The Raman spectra of vanillin in CCl_4 solution (upper) and in aqueous solution (lower).

TABLE LXXII

SPECTRAL DATA - SOLVENTS

CS_2 Infrared, cm^{-1}	CCl_4 Infrared, cm^{-1}	CCl_4 Raman, cm^{-1}
521 ms[a]		219 m
1463 ms		314 m
1485 s		460 s
1488 s	518 s	
1528 s	760 vs	760 w
1546 s	786 vs	788 w
2155 m	979 w	
	1005 w	
	1218 w	
Methanol Raman, cm^{-1}	1254 w	
		1533 vw
	1550 w	
465 vw		1575 vw
486 vw		
1034 m		
1111 vw	Water Raman, cm^{-1}	
1155 vw		
1451 w	3252 sh	
1467 w	3406 s	
2831 s		
2916 sh		
2941 s		
2978 sh		
3330 w		

[a]Strong (s), medium (m), weak (w), shoulder (sh), very (v).

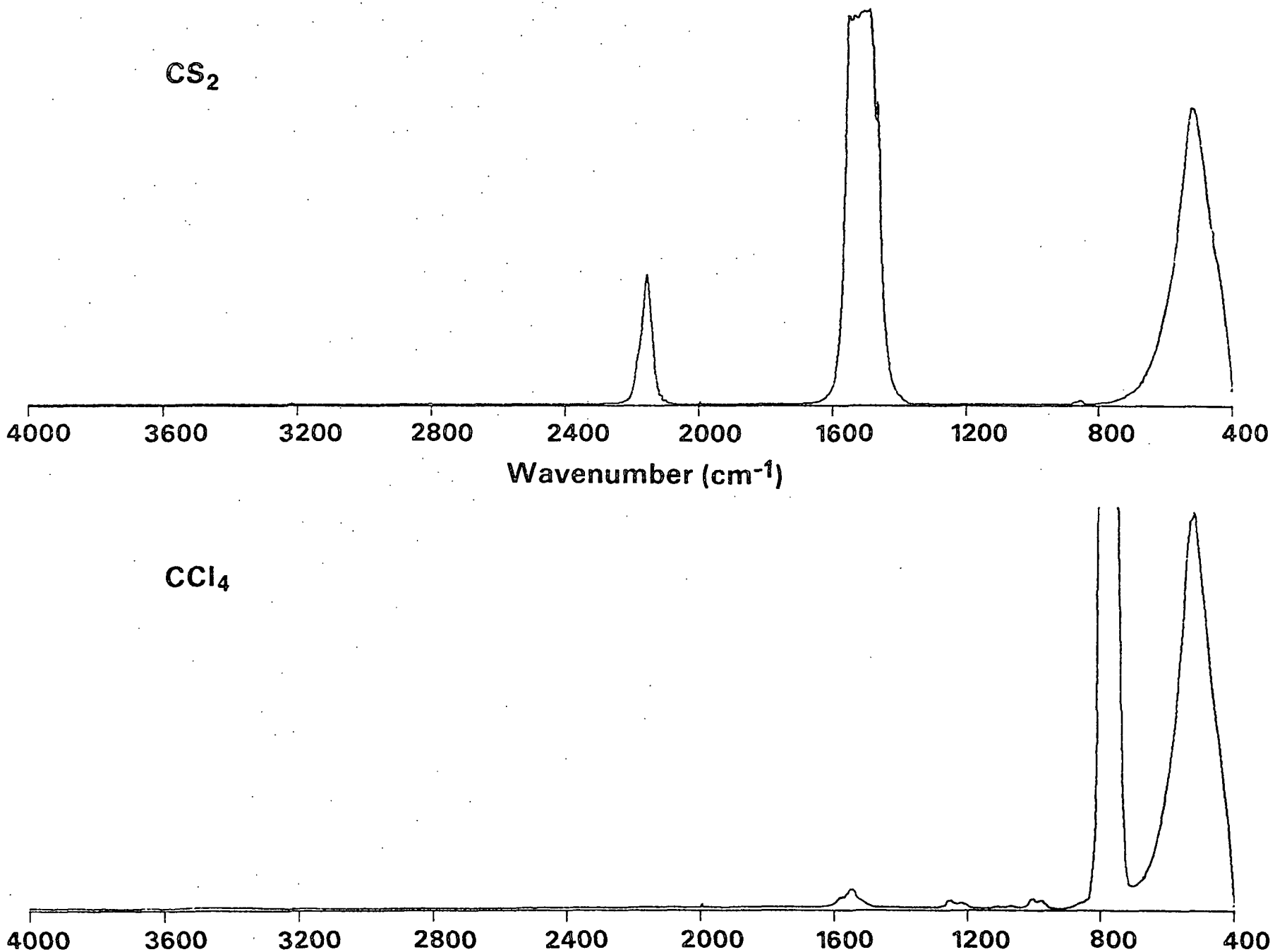


Figure 52. The IR spectra of CS_2 and CCl_4.

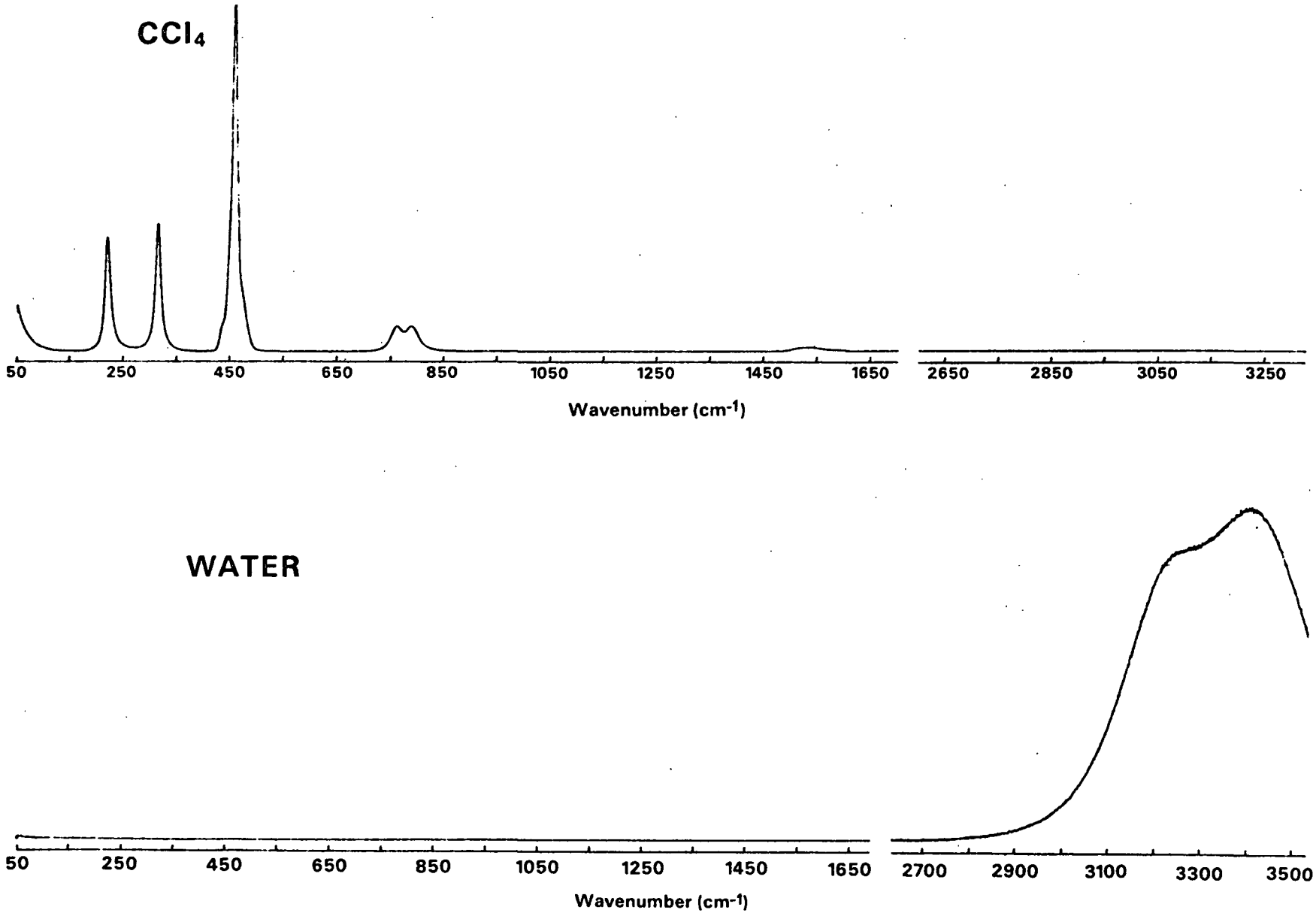


Figure 53. The Raman spectra of CCl_4 and H_2O.

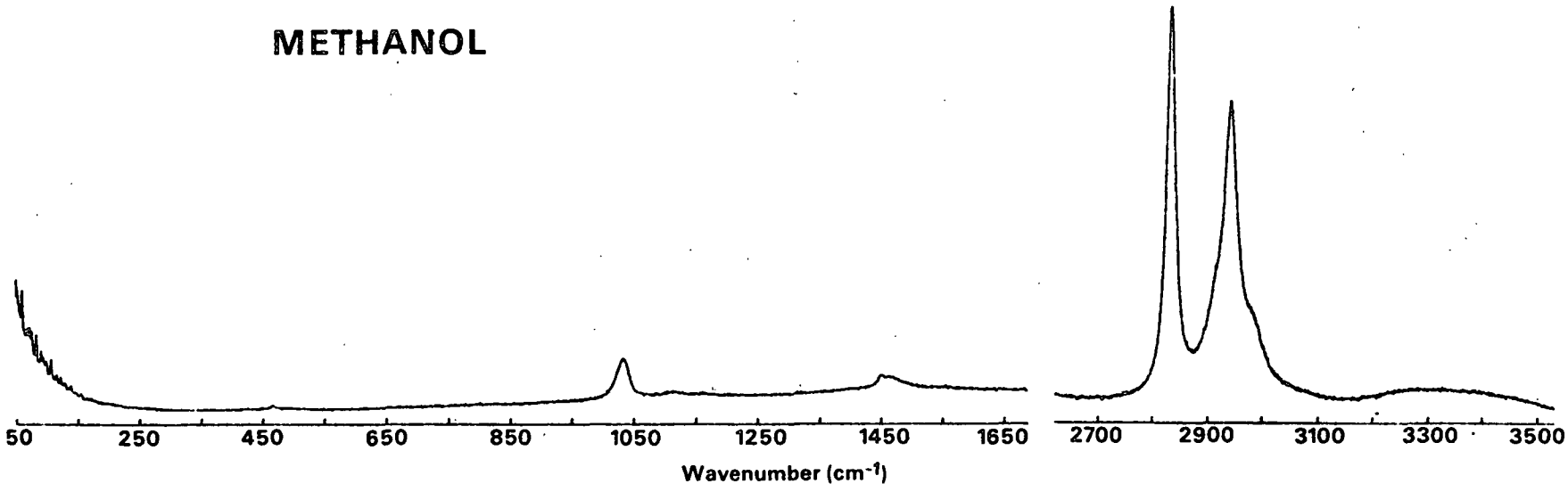


Figure 54. The Raman spectra of MeOH.

APPENDIX IV

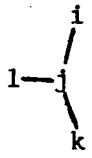
DEFINITION OF THE INTERNAL COORDINATES FOR THE MODEL COMPOUNDS

The normal modes of a polyatomic molecule can be completely described using five different types of internal coordinates. Only four different types of internal coordinates are needed to define the vibrations of the benzene derivatives: bond stretches, angle bends, out-of-plane wags and torsions.

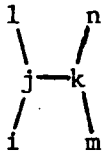
These are defined as follows:

Bond stretch, i-j: change in the length of the bond joining atoms i and j.

Angle bend, i-j-k: change in the angle defined by the two bonds ij and jk.



Out-of-plane wag, l-jik: change in the angle between the jl bond and the plane defined by atoms i, j and k.

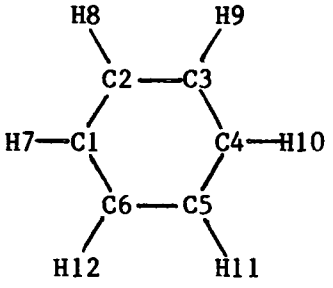


Torsion, ljkm: change in the angle between the plane defined by atoms ljk and the plane defined by atoms jkm. In these calculations all torsions are defined as linear combinations of two or more torsions about the bond, e.g., as ijkn + ljkm. Such sums are normalized.

The definitions of these internal coordinates for the model compounds are presented in Tables LXXIII-LXXX.

TABLE LXXIII

INTERNAL COORDINATE DEFINITIONS FOR BENZENE



IN-PLANE

Bond Stretches

1. C1-C2	5. C5-C6	9. C3-H9
2. C2-C3	6. C6-C1	10. C4-H10
3. C3-C4	7. C1-H7	11. C5-H11
4. C4-C5	8. C2-H8	12. C6-H12

Angle Bends

13. H7-C1-C2	19. H10-C4-C5	25. C6-C1-C2
14. C1-C2-H8	20. C4-C5-H11	26. C1-C2-C3
15. H8-C2-C3	21. H11-C5-C6	27. C2-C3-C4
16. C2-C3-H9	22. C5-C6-H12	28. C3-C4-C5
17. H9-C3-C4	23. H12-C6-C1	29. C4-C5-C6
18. C3-C4-H10	24. C6-C1-H7	30. C5-C6-C1

OUT-OF-PLANE

Wags

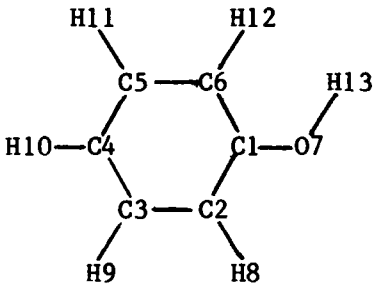
1. H7-C1C6C2	3. H9-C3C2C4	5. H11-C5C4C6
2. H8-C2C1C3	4. H10-C4C3C5	6. H12-C6C5C1

Torsions

7. H7C1C2C3 + C6C1C2H8	9. H9C3C4C5 + C2C3C4H10	11. H11C5C6C1 + C4C5C6H12
8. H8C2C3C4 + C1C2C3H9	10. H10C4C5C6 + C3C4C5H11	12. H12C6C1C2 + C5C6C1H7

TABLE LXXIV

INTERNAL COORDINATE DEFINITIONS FOR PHENOL



IN-PLANE

Bond Stretches

1.	C1-C2	6.	C6-C1	10.	C5-H11
2.	C2-C3	7.	C2-H8	11.	C6-H12
3.	C3-C4	8.	C3-H9	28.	C1-O7
4.	C4-C5	9.	C4-H10	29.	O7-H13
5.	C5-C6				

Angle Bends

12.	C1-C2-H8	19.	H11-C5-C6	25.	C3-C4-C5
13.	H8-C2-C3	20.	C5-C6-H12	26.	C4-C5-C6
14.	C2-C3-H9	21.	H12-C6-C1	27.	C5-C6-C1
15.	H9-C3-C4	22.	C6-C1-C2	30.	C6-C1-O7
16.	C3-C4-H10	23.	C1-C2-C3	31.	O7-C1-C2
17.	H10-C4-C5	24.	C2-C3-C4	32.	C1-O7-H13
18.	C4-C5-H11				

OUT-OF-PLANE

Wags

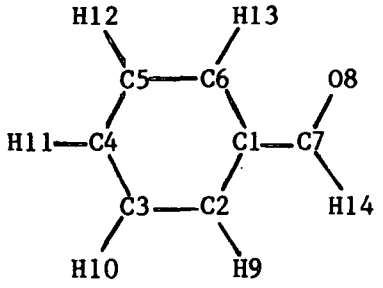
1.	H8-C2C1C3	3.	H10-C4C3C5	5.	H12-C6C5C1
2.	H9-C3C2C4	4.	H11-C5C4C6	12.	O7-C1C6C2

Torsions

6.	O7C1C2C3 + C6C1C2H8	9.	H10C4C5C6 + C3C4C5H11	11.	H12C6C1C2 + C5C6C1O7
7.	H8C2C3C4 + C1C2C3H9	10.	H11C5C6C1 + C4C5C6H12	13.	C2C1O7H13 + C6C1O7H13
8.	H9C3C4C5 + C2C3C4H10				

TABLE LXXV

INTERNAL COORDINATE DEFINITIONS FOR BENZALDEHYDE



IN-PLANE

Bond Stretches

1.	C1-C2	6.	C6-C1	11.	C6-H13
2.	C2-C3	7.	C2-H9	28.	C1-C7
3.	C3-C4	8.	C3-H10	29.	C7-O8
4.	C4-C5	9.	C4-H11	30.	C7-H14
5.	C5-C6	10.	C5-H12		

Angle Bends

12.	C1-C2-H9	19.	H12-C5-C6	26.	C4-C5-C6
13.	H9-C2-C3	20.	C5-C6-H13	27.	C5-C6-C1
14.	C2-C3-H10	21.	H13-C6-C1	31.	C6-C1-C7
15.	H10-C3-C4	22.	C6-C1-C2	32.	C7-C1-C2
16.	C3-C4-H11	23.	C1-C2-C3	33.	C1-C7-O8
17.	H11-C4-C5	24.	C2-C3-C4	34.	O8-C7-H14
18.	C4-C5-H12	25.	C3-C4-C5	35.	H14-C7-C1

OUT-OF-PLANE

Wags

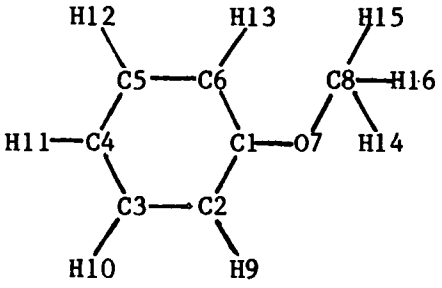
1.	H9-C2C1C3	4.	H12-C5C4C6	13.	O8-C7C1H14
2.	H10-C3C2C4	5.	H13-C6C5C1	14.	H14-C7C1O8
3.	H11-C4C3C5	12.	C7-C1C6C2		

Torsions

6.	C7C1C2C3 + C6C1C2H9	9.	H11C4C5C6 + C3C4C5H12	11.	H13C6C1C2 + C5C6C1C7
7.	H9C2C3C4 + C1C2C3H10	10.	H12C5C6C1 + C4C5C6H13	15.	C2C1C7O8 + C6C1C7H14
8.	H10C3C4C5 + C2C3C4H11				

TABLE LXXVI

INTERNAL COORDINATE DEFINITIONS FOR ANISOLE



IN-PLANE

Bond Stretches

1.	C1-C2	7.	C2-H9	28.	C1-O7
2.	C2-C3	8.	C3-H10	29.	O7-C8
3.	C3-C4	9.	C4-H11	30.	C8-H14
4.	C4-C5	10.	C5-H12	31.	C8-H15
5.	C5-C6	11.	C6-H13	32.	C8-H16
6.	C6-C1				

Angle Bends

12.	C1-C2-H9	21.	H13-C6-C1	34.	O7-C1-C2
13.	H9-C2-C3	22.	C6-C1-C2	35.	C1-O7-C8
14.	C2-C3-H10	23.	C1-C2-C3	36.	O7-C8-H14
15.	H10-C3-C4	24.	C2-C3-C4	37.	O7-C8-H15
16.	C3-C4-H11	25.	C3-C4-C5	38.	O7-C8-H16
17.	H11-C4-C5	26.	C4-C5-C6	39.	H15-C8-H16
18.	C4-C5-H12	27.	C5-C6-C1	40.	H16-C8-H14
19.	H12-C5-C6	33.	C6-C1-O7	41.	H14-C8-H15
20.	C5-C6-H13				

OUT-OF-PLANE

Wags

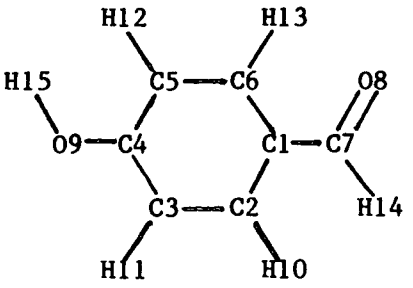
1.	H9-C2C1C3	3.	H11-C4C3C5	5.	H13-C6C5C1
2.	H10-C3C2C4	4.	H12-C5C4C6	12.	O7-C1C6C2

Torsions

6.	O7C1C2C3 + C6C1C2H9	9.	H11C4C5C6 + C3C4C5H12	13.	C6C1O7C8 + C2C1O7C8
7.	H9C2C3C4 + C1C2C3H10	10.	H12C5C6C1 + C4C5C6H13	14.	C1O7C8H14 + C1O7C8H15
8.	H10C3C4C5 + C2C3C4H11	11.	H13C6C1C2 + C5C6C1O7		+ C1O7C8H16

TABLE LXXVII

INTERNAL COORDINATE DEFINITIONS FOR 4-HYDROXYBENZALDEHYDE



IN-PLANE

Bond Stretches

1.	C1-C2	6.	C6-C1	25.	C1-C7
2.	C2-C3	7.	C2-H10	26.	C7-O8
3.	C3-C4	8.	C3-H11	27.	C7-H14
4.	C4-C5	9.	C5-H12	33.	C4-O9
5.	C5-C6	10.	C6-H13	34.	O9-H15

Angle Bends

11.	C1-C2-H10	19.	C6-C1-C2	29.	C7-C1-C2
12.	H10-C2-C3	20.	C1-C2-C3	30.	C1-C7-O8
13.	C2-C3-H11	21.	C2-C3-C4	31.	O8-C7-H14
14.	H11-C3-C4	22.	C3-C4-C5	32.	H14-C7-C1
15.	C4-C5-H12	23.	C4-C5-C6	35.	C3-C4-O9
16.	H12-C5-C6	24.	C5-C6-C1	36.	O9-C4-C5
17.	C5-C6-H13	28.	C6-C1-C7	37.	C4-O9-H15
18.	H13-C6-C1				

OUT-OF-PLANE

Wags

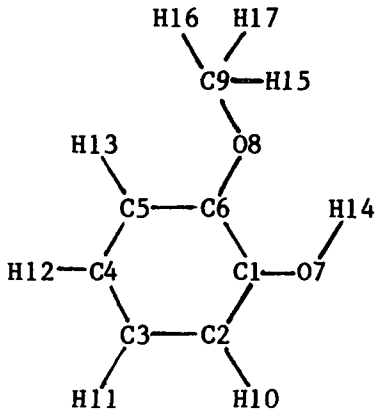
1.	H10-C2C1C3	4.	H13-C6C5C1	13.	H14-C7C1O8
2.	H11-C3C2C4	11.	C7-C1C6C2	15.	O9-C4C3C5
3.	H12-C5C4C6	12.	O8-C7C1H14		

Torsions

5.	C7C1C2C3 + C6C1C2H10	8.	O9C4C5C6 + C3C4C5H12	14.	C2C1C7O8 + C6C1C7H14
6.	H10C2C3C4 + C1C2C3H11	9.	H12C5C6C1 + C4C5C6H13	16.	C3C4O9H15 + C5C4O9H15
7.	H11C3C4C5 + C2C3C4O9	10.	H13C6C1C2 + C5C6C1C7		

TABLE LXXVIII

INTERNAL COORDINATE DEFINITIONS FOR GUAIACOL



IN-PLANE

Bond Stretches

1.	C1-C2	7.	C2-H10	30.	C6-O8
2.	C2-C3	8.	C3-H11	31.	O8-C9
3.	C3-C4	9.	C4-H12	32.	C9-H15
4.	C4-C5	10.	C5-H13	33.	C9-H16
5.	C5-C6	25.	C1-O7	34.	C9-H17
6.	C6-C1	26.	O7-H14		

Angle Bends

11.	C1-C2-H10	18.	H13-C5-C6	27.	C6-C1-O7	38.	O8-C9-H15
12.	H10-C2-C3	19.	C6-C1-C2	28.	O7-C1-C2	39.	O8-C9-H16
13.	C2-C3-H11	20.	C1-C2-C3	29.	C1-O7-H14	40.	O8-C9-H17
14.	H11-C3-C4	21.	C2-C3-C4	35.	C5-C6-O8	41.	H16-C9-H17
15.	C3-C4-H12	22.	C3-C4-C5	36.	O8-C6-C1	42.	H17-C9-H15
16.	H12-C4-C5	23.	C4-C5-C6	37.	C6-O8-C9	43.	H15-C9-H16
17.	C4-C5-H13	24.	C5-C6-C1				

OUT-OF-PLANE

Wags

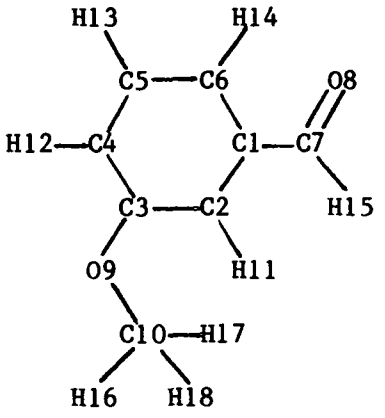
1.	H10-C2C1C3	3.	H12-C4C3C5	11.	O7-C1C6C2
2.	H11-C3C2C4	4.	H13-C5C4C6	13.	O8-C6C5C1

Torsions

5.	O7C1C2C3 + C6C1C2H10	8.	H12C4C5C6 + C3C4C5H13	12.	C6C1O7H14 + C2C1O7H14
6.	H10C2C3C4 + C1C2C3H11	9.	H13C5C6C1 + C4C5C6O8	14.	C5C6O8C9 + C1C6O8C9
7.	H11C3C4C5 + C2C3C4H12	10.	O8C6C1C2 + C5C6C1O7	15.	C6O8C9H15 + C6O8C9H16 + C6O8C9H17

TABLE LXXIX

INTERNAL COORDINATE DEFINITIONS FOR m-ANISALDEHYDE



IN-PLANE

Bond Stretches

1.	C1-C2	6.	C6-C1	25.	C1-C7	34.	O9-C10
2.	C2-C3	7.	C2-H11	26.	C7-O8	35.	C10-H16
3.	C3-C4	8.	C4-H12	27.	C7-H15	36.	C10-H17
4.	C4-C5	9.	C5-H13	33.	C3-O9	37.	C10-H18
5.	C5-C6	10.	C6-H14				

Angle Bends

11.	C1-C2-H11	18.	H14-C6-C1	28.	C6-C1-C7	40.	C3-O9-C10
12.	H11-C2-C3	19.	C6-C1-C2	29.	C7-C1-C2	41.	O9-C10-H16
13.	C3-C4-H12	20.	C1-C2-C3	30.	C1-C7-O8	42.	O9-C10-H17
14.	H12-C4-C5	21.	C2-C3-C4	31.	O8-C7-H15	43.	O9-C10-H18
15.	C4-C5-H13	22.	C3-C4-C5	32.	H15-C7-C1	44.	H17-C10-H18
16.	H13-C5-C6	23.	C4-C5-C6	38.	C2-C3-O9	45.	H18-C10-H16
17.	C5-C6-H14	24.	C5-C6-C1	39.	O9-C3-C4	46.	H16-C10-H17

OUT-OF-PLANE

Wags

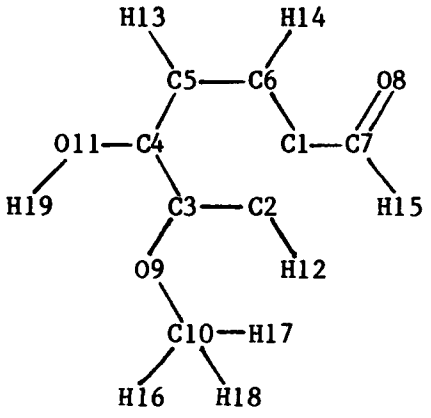
1.	H11-C2C1C3	4.	H14-C6C5C1	13.	H15-C7C1O8
2.	H12-C4C3C5	11.	C7-C1C6C2	15.	O9-C3C2C4
3.	H13-C5C4C6	12.	O8-C7C1H15		

Torsions

5.	C7C1C2C3 + C6C1C2H11	8.	H12C4C5C6 + C3C4C5H13	14.	C2C1C7O8 + C6C1C7H15
6.	H11C2C3C4 + C1C2C3O9	9.	H13C5C6C1 + C4C5C6H14	16.	C2C3O9C10 + C4C3O9C10
7.	O9C3C4C5 + C2C3C4H12	10.	H14C6C1C2 + C5C6C1C7	17.	C3O9C10H16 + C3O9C10H17 + C3O9C10H18

TABLE LXXX

INTERNAL COORDINATE DEFINITIONS FOR VANILLIN



IN-PLANE

Bond Stretches

1.	C1-C2	6.	C6-C1	23.	C7-O8	33.	C10-H17
2.	C2-C3	7.	C2-H12	24.	C7-H15	34.	C10-H18
3.	C3-C4	8.	C5-H13	30.	C3-O9	44.	C4-O11
4.	C4-C5	9.	C6-H14	31.	O9-C10	45.	O11-H19
5.	C5-C6	22.	C1-C7	32.	C10-H16		

Angle Bends

10.	C1-C2-H12	18.	C2-C3-C4	28.	O8-C7-H15	40.	O9-C10-H18
11.	H12-C2-C3	19.	C3-C4-C5	29.	H15-C7-C1	41.	H17-C10-H18
12.	C4-C5-H13	20.	C4-C5-C6	35.	C2-C3-O9	42.	H18-C10-H16
13.	H13-C5-C6	21.	C5-C6-C1	36.	O9-C3-C4	43.	H16-C10-H17
14.	C5-C6-H14	25.	C6-C1-C7	37.	C3-O9-C10	46.	C3-C4-O11
15.	H14-C6-C1	26.	C7-C1-C2	38.	O9-C10-H16	47.	O11-C4-C5
16.	C6-C1-C2	27.	C1-C7-O8	39.	O9-C10-H17	48.	C4-O11-H19
17.	C1-C2-C3						

OUT-OF-PLANE

Wags

1.	H12-C2C1C3	3.	H14-C6C5C1	11.	O8-C7C1H15	14.	O9-C3C2C4
2.	H13-C5C4C6	10.	C7-C1C6C2	12.	H15-C7C1O8	17.	O11-C4C3C5

Torsions

4.	C7C1C2C3 + C6C1C2H12	7.	O11C4C5C6 + C3C4C5H13	13.	C6C1C7H15 + C2C1C7O8	16.	C3O9C10H16 + C3O9C10H17 + C3O9C10H18
5.	H12C2C3C4 + C1C2C3O9	8.	H13C5C6C1 + C4C5C6H14	15.	C2C3O9C10 + C4C3O9C10	18.	C3C4O11H19 + C5C4O11H19
6.	O9C3C4C5 + C2C3C4O11	9.	H14C6C1C2 + C5C6C1C7				

APPENDIX V

INSTRUCTIONS FOR RUNNING THE NORMAL COORDINATE CALCULATION PROGRAMS ON THE BURROUGHS 6900 COMPUTER

CART

The operation of CART requires a data file titled CART/DATA or if otherwise titled, specified in a file statement. This data file must contain the following data:

1. -09, problem ID card.

2. Problem control card. Typed in free format.
   IND,NOAT,NISO,NOPT,IFPUN
   - IND = -09, signifies the problem control card.
   - NOAT, the number of atoms in the molecule.
   - NISO, the number of additional isotopically substituted molecules. If no isotopically substituted molecules are to be included a zero should be entered.
   - NOPT is the punch and moment of inertia control card.
     - = -1, both the standard and principal cartesian coordinates are computed and entered in a file titled CART/OUTPUT.
     - = 0, both the standard and the principal cartesian coordinates are entered in CART/OUTPUT if IFPUN = 1.
     - = 1, only the standard cartesian coordinates are computed and are entered in CART/OUTPUT.
   - IFPUN must be equal to 1 for the principal cartesian coordinates to be entered in CART/OUTPUT regardless of the value of NOPT.

3. The next two cards are the problem information cards. These lines contain any alphanumeric information about the problem that the user may wish to include. These two lines must be entered even if left blank.

4. Atom definition cards. One for each atom of the molecule in the order of NO = 1,2,3,...,NOAT. Typed in free format.
   NO,NA,NB,NC,R,TE,PH,WT
   - NO, the number of the atom being defined
   - NA, NB, and NC, the numbers referring to atoms A,B and C. NA, NB, and NC must be less than NO.
   - R, the distance between atom NO and atom NA, i.e., the bond length NO-NA
   - TE, the angle between atoms NO, NA, and NB, i.e., the bond angle NO-NA-NB. If TE is set equal to zero, the angle is assumed to be tetrahedral.
   - PH, the dihedral angle between the planes defined by atoms NO, NA, NB and NA, NB, and NC.
   - WT, the mass of atom NO. This information is only required if the center of mass is to be computed.
   - These atom definition cards must be in the order of NO = 1,2,3,...,NOAT. NA, NB and NC must be less than NO.

5. -06 followed by any alphanumeric information. If NISO is greater than zero, a mass ID card for each isotopically substituted molecule must follow the atom definition cards. If NISO is zero these lines are omitted.

6. The masses of the atoms in the isotopically substituted molecule follow the mass ID card in the order 1,2,3,...,NOAT. The masses are input six per card with a comma separating each (free format).

7. 999,0,0,0,0
   Data termination card, designates the end of the data file.

   All output goes to the printer. Cartesian coordinates, as specified by NOPT, are also output to a file titled CART/OUTPUT.

GMAT

To run GMAT a data file titled GMAT/DATA or specified in a file statement is necessary. This data file must contain the following data in free format (unless otherwise specified):

1. -09, problem ID card.

2. Problem control card.
   IND,NOPROB,NOAT,NQ,INTC,NISO,IFB,NCON
   - IND = -09, identifies the problem control card.
   - NOPROB, the problem number.
   - NOAT, the number of atoms in the molecule.
   - NQ, the number of internal coordinates.
   - INTC = 1, the unsymmetric G matrix will be written into the output file GMAT/OUTPUT.
   - NISO, the number of isotopically substituted molecules included in the problem.
   - IFB, B matrix suppression option.
     - = -1, B and G matrices are not printed and not written to the output file, GMAT/OUTPUT.
     - = 0, the B matrix is printed but not written in the output file, the G matrix is controlled by NCON.
     - = 1, the B and G matrices are printed and written to the output file, GMAT/OUTPUT if NCON = 0.
   - NCON, output suppresssion option.
     - = 1, all output, both to printer and to output file is suppressed except for the printout of the symmetric G matrix.
     - = 0, no suppression.

3. Problem information cards. Two are required. They contain any desired alphanumeric information about the problem and must be included even if left blank.

4. Cartesian coordinates. Either standard or principal cartesian coordinates can be used. These coordinates are read as output by CART [FORMAT 4(2I3,F12.6)]. The row number following the last coordinate must be -1.

5. Internal coordinate definitions. The internal coordinates are defined by "vectors" containing eight numbers:
   NI,NCOD,N1,N2,N3,N4,N5,N6
   - NI, the number assigned to the internal coordinate.
   - NCOD, the code identifying the type of internal coordinate.
   - N1-N6, the numbers of the atoms defining the coordinate.

   A description of the internal coordinate coding system can be found in Pitzner's thesis (136) or in Schachtschneider's manual (135). The internal coordinates must be defined in order 1 through NQ. Three such vectors are input per line in free format. A final vector with NI = -02 is needed to designate the end of the internal coordinate information. If NI = 0, the vector is added to the previous vector.

6. Isotope control card.
   IN = -06, identifies the isotope control card and is entered in columns 1-3.
   IFU, U matrix read option control, entered in columns 4-6.
   = -1, the U matrix is not entered with the input, but the G matrix is symmetrized with the U matrix from the previous isotopically substituted molecule.
   = 0, the U matrix is not included with the input and the G matrix is not symmetrized.
   = 1, the U matrix is entered and the G matrix symmetrized.
   NSB, the number of factored blocks or symmetry species plus 1. Entered in columns 7-10.
   NS, the number of symmetry coordinates, entered in columns 11-12.
   Any alphanumeric information concerning this molecule may be input on the remainder of this line.

7. Atomic masses, entered in free format, six/line in order 1 through NOAT.

8. U matrix. If IFU = 1, the U matrix is entered next. The row, column and value of each element are typed in free format with four elements/line. It is not necessary to include zero elements. Nor is it necessary for the matrix to be normalized. Row elements must be entered in order. The row number following the last element should be set equal to -3.

9. Symmetry block information. If IFU = 1, the next line contains the numbers of the first row of each factored block in free format. NSB numbers are required. The last number should be NS + 1.

10. Data termination card.
    999000000000
    If another problem is to be included with the input data, the problem ID card of the next set of data is placed at this point in place of the data termination card.

All output goes to the printer. The B, G and symmetrized G are also output to a file titled GMAT/OUTPUT as specified in problem control card.

UBZM

To set up a Z matrix UBZM requires a data file titled UBZM/DATA or otherwise specified in a file statement. The data file must have the following information.

1. Problem control card. Typed in free format.
   IND,NOPROB,NOAT,NCOR,NF,IFF,NOFF,INFRA,PUNCH,NOX
   - IND = -09, indicates the start of a problem.
   - NOPROB, the problem number.
   - NOAT, the number of atoms. (<26)
   - NCOR, the number of internal coordinates.
   - NF, the number of force constants.
   - IFF = 1, signifies that the force constants are included with the input and that the F matrix is to be evaluated.
   - NOFF, the number of non-Urey-Bradley constants to be specified or the number of MVFF interaction constants.
   - INFRA = 1, causes the intermediate GEM, TETRA, and CIS matrices (UBFF) to be printed.
   - PUNCH = 1, suppresses output of the Z matrix to the UBZM/OUTPUT file
   - NOX = 1, the cartesian coordinates are not read in and the atom distance check is not computed. For UBFF calculations NOX must be 0.

2. Problem information cards. Two lines of any alphanumeric information about the problem must be included even if blank.

3. Cartesian coordinates. If NOX = 0, the cartesian coordinates are input at this point. They are input as output by CART. [FORMAT 4(2I3,F12.6)].

4. Diagonal force constants. The position of the element (row or column number) and force constant parameter number of the diagonal elements of the UBFF or MVFF are specified, twelve/line, in free format.

5. Interaction force constants. The row, column and force constant parameter numbers for each of the off-diagonal elements of the MVFF or for each non-Urey-Bradley interaction constant are specified, eight/line in free format.

6. Two blank lines. For the computation of a UBFF configuration "vectors" are placed at this point followed by 2 blank lines. For a MVFF just 2 blank lines (30 zeros in free format) are necessary.

7. Force constant parameters. If IFF = 1, i.e., the F matrix is to be evaluated, the force constant parameters are included in the data file at this point, 6 constants/line, separated by commas.

8. Data termination card.
   999,0,0,0,0,0,0,0,0,0

   The problem control card of a new problem may also be placed at this position.

All output goes to the printer. The Z matrix is also output to the file UBZM/OUTPUT if specified by PUNCH.

ZSYM

To symmetrize the Z matrix ZSYM requires a data file titled ZSYM/DATA or otherwise specified in a file statement. The data file should contain:

1. Problem control card, typed in free format.
   IND,NQ,NF,NS,NSB,IFSK,IFREP,NST,FPUN
   - IND = -09, indicates the start of a problem.
   - NQ, the number of internal coordinates.
   - NF, the number of force constant parameters.
   - NS, the number of symmetry coordinates.
   - NSB, the number of factored blocks plus 1.
   - IFSK, polymer control option.
     - = 0 for a normal molecule. Only one U matrix is read in.
     - = 1 for a polymer. Two U matrices, U and U are read in.
   - IFREP, repeat option control.
     - = 0 for a new problem. New Z and U matrices are read in.
     - = 1, a new Z matrix is entered, but the U matrix from the previous problem is used for symmetrization.
   - NST, starting index for the DO loop on force constants. This constant must be entered when IFREP = 1, otherwise, NST = 0.
   - FPUN = 1, the factored Z matrix is not read into the ZYSM/OUTPUT file.

2. Problem information cards. Two lines containing any desired alphanumeric information about the problem or left blank.

3. Z matrix. The Z matrix is input as output by UBZM: four elements/line, each element consisting of a row number, a column number, a force constant parameter number and a numerical Z matrix element [FORMAT 4(3I3,F9.6)]. The row number after the last element must be -2.

4. U matrix. Input with four elements/line, each element consisting of a row number, column number and U matrix element in free format. Zero elements need not be included. The matrix does not need to be normalized.

5. U matrix. If IFSK = 1, the second U matrix must follow the first, with the same format as the first.

6. Symmetry block information. Input the row numbers of the first row of each factored block in free format. The last element should be NS + 1.

7. Data termination card.
   999,0,0,0,0,0,0,0,0
   Problem control card of a new problem may be placed in this position instead of the data termination card.

All output goes to the printer. The symmetrized Z matrix is also written to a file titled ZSYM/OUTPUT if FPUN = 0.

FLPO

The data file for FLPO must be titled FLPO/DATA or if otherwise titled, specified in a file statement. The data file should contain the following information:

1. Problem ID card.
   -09

2. Problem control card, typed in free format.
   IND,NOPROB,NMOL,NF,NPMAX,NCZ,IFREP,IFER,PER,EST,EPS,RAP,FRAC,
   LEAP,CONV,IFDEL

   IND = -09, identifies problem control card.
   NOPROB, the problem number.
   NMOL, the number of molecules.
   NF, the number of force constant parameters.
   NPMAX, the maximum number of desired iterations. The refinement will terminate when NPMAX is exceeded even if convergence has not been reached. If NPMAX = 0 the frequencies will be calculated for the problem based on the initial set of parameters and there will be no refinement of the force constant parameters.
   NCZ, the number of force constants to be held fixed. These force constants do not enter the refinement. Their final value is identical to their initial value.
   IFREP, the problem repeat option.
   = 0, a new problem is started.
   = 1, only a new set of force constants and a list of those force constants to be held fixed are read in, the rest of the problem information is taken from the previous problem.
   = -1, the final set of force constants from the previous problem are used as the initial set in the new problem, the rest of the problem data must be included with the input data.
   IFER, error option control.
   = 1, the fractional error in the experimental frequencies, PER, is read in.
   = 0, the fractional error, PER, is assumed to be 0.005.
   = -1, the estimated errors in the frequencies, in cm^{-1}, are read in.
   = -3, the error is assumed to be PER = 1.0 cm^{-1}.
   PER, the fractional error in the experimental frequencies. Specified if IFER = 1, set equal to zero otherwise.
   EST, estimate of the value of the weighted sum of squares of the residuals at the minimum. If a value cannot be estimated for EST, it is set equal to zero.
   EPS, test value representing the expected absolute error. A reasonable value for EPS is 0.1E-05.
   RAP, the cutoff factor for the Jacobi diagonalization. The plane rotations are terminated when MAX[H(I,J)] is less than RAP*MIN[H(I,I)]. If RAP is set to zero, the program assigns a value of 0.5E-2. On the final cycle, RAP is set equal to 0.5E-3 which results in eigenvalues significant to six figures and eigenvectors significant to 3 or 4 figures.

FRAC, a fractional factor for decreasing RAP on each cycle. After each perturbation, RAP is set equal to FRAC*RAP. If FRAC = 0 it is assumed to be 0.9.

LEAP = 1 suppresses printout of eigenvalues and errors, gradient vector, argument vector, direction vector, argument difference vector, and gradient difference vector for each perturbation.

CONV, convergence criterion. The refinement will terminate when the corrections to the force constant parameters are all less than or equal to the absolute value of CONV. A value of 0.0001 is suggested by Pitzner ( ).

IFDEL = 1, the difference between the calculated and observed frequencies are printed out for each perturbation. IFDEL may be set equal to 1 only when NMOL = 1.

3. Problem information cards. Three lines containing any alphanumeric information about the problem or left blank are required.

4. Initial force constant values are entered next, in free format, six per line.

5. Force constants to be held fixed. If NCZ > 0, the numbers of the force constants to be held fixed are entered in free format, 24/line.

6. Molecule control card, typed in free format.
IND,NQ,NDD,NZZ,IFU,IFW,ISKZ,STUT,RATIO,ITERM

IND = -06, identifies the molecule control card.

NQ, the number of internal coordinates.

NDD, the number of nonzero experimental frequencies included with the input data. If NPMAX = 0 the experimental frequencies need not be included (NDD = 0).

NZZ, the number of Z matrix elements.

IFU = 1, designates printout of the final H matrix.

IFW, weighting element option for the weighted least squares refinement.

= 2, the weighting elements, E(I), are read i, one for each nonzero experimental frequency. Weight(I) = E(I).

= 1, the weighting elements, E(I), are read in, one for each nonzero experimental frequency. Weight(I) = E(I)/frequency parameter(I).

= 0, weight(I) = 1/frequency parameter(I).

= -1, weight is equal to 1.0 for all frequencies.

= -3, weight(I) = 1/[frequency parameter(I)].

ISKZ, Z matrix repeat option.

= 0, the Z matrix is included with the input data.

= 1, the Z matrix from the previous problem is used.

STUT, value from Student's t distribution needed to compute the 95% confidence intervals for the final set of force constants. STUT t(n-p,0.975), where n=NDD, the number of nonzero experimental frequencies, and p=NF-NCZ, the number of force constant parameters being refined. If STUT = 1.0, the standard errors in the force constants are printed instead of the 95% confidence intervals.

RATIO, defines another criterion to judge the convergence of the refinement and upon which to base termination of the refinement.

A reasonable value for RATIO is suggested by Pitzner to be 0.995. When the ratio of successive weighted sums of squares is equal to or greater than RATIO, the force constant refinement will be terminated and said to have converged if the condition has previously been met ITERM times.

ITERM, the number of times RATIO must be equaled or exceeded before the refinement is terminated.

7. Molecule information card. One line containing the name of the molecule, other alphanumeric information, or blank is included at this point.

8. Z matrix. Input as output by UBZM or ZSYM [FORMAT 4(3I3,F9.6)]. The row number of the element following the last Z matrix element must be set equal to -2.

9. Experimental frequencies. If NDD > 0, the experimental frequencies, in cm^{-1}, are included with the input data. The frequencies are entered in decreasing order in free format. For NDD > 0, there must be NQ frequencies entered NDD of which must be nonzero. Any frequency may be given a zero weight in the refinement by entering a zero instead of the actual frequency.

10. Estimated errors in the experimental frequencies. If IFER = -1, the estimated error in the observed frequencies, in cm^{-1}, must be included with the input data, one for each nonzero frequency. The estimated errors are entered in the same order as the experimental frequencies, with zeros corresponding to zeros in the list of experimental frequencies. For IFER = -1, there must be NQ error entries, NDD of them nonzero. Typed in free format.

11. Weighting elements. If IFW = -2 or 1, the weighting elements must be included with the data file, one element for each nonzero frequency. There should be NDD weighting elements which must be arranged in the same order as the nonzero experimental frequencies. Typed in free format.

12. G matrix. Input in same format as output from GMAT [FORMAT 4(2I3,F12.6)]. The row number following the last G matrix element must be -1.

13. Data termination card.
999

If another problem is to be included in the data file this problem ID card for the next problem should be placed at this point.

All specified output goes to the printer. The refined values of the force constants are also written to the file FLPO/OUTPUT.

EIGV

To run EIGV a data file titled EIGV/DATA is needed, or if otherwise titled, identified in a file statement. The data file should include the following:

1. Problem ID card.
   -09

2. Problem control card, typed in free format.
   IND,NOPROB,NMOL,NF,INO,IEG,IFF,RAP
   IND = -09, identifies the problem control card.
   NORPOB, the problem number.
   NMOL, the number of molecules.
   NF, the number of force constants.
   INO, the number of force constants to be renumbered.
   IEG = 1, the problem is terminated after the secular equation has been solved and the eigenvalues determined.
   IFF = 1 causes print out of the F matrix.
   RAP, cutoff factor for Jacobi diagonalization. The plane rotations are terminated when MAX[H(I,J)] is less than RAP*MIN[H(I,I)]. If RAP = 0.0 a value of 0.5E-3 is assumed.

3. Problem information cards. Three lines containing alphanumeric information about the problem are required. These lines may be left blank, but must be included.

4. Force constants. Read in order 1 through NF in free format.

5. Force constants to be renumbered. If INO > 0, the force constants to be renumbered are entered with the old force constant number listed first followed by the new number. INO sets of numbers, 24/line are entered in free format.

6. Molecule control card, typed in free format.
   IND,NQ,NDD,NZZ,IFU,IFW,ISKZ,IFINV,IFMA,IFB,NOAT,IFCOR,NOTEP,
   SCALE,ICAR,IMSC,ICOR,ITEMP,ABST,ICD,IPUN,IFL
   IND = -06, identifies the molecule control card.
   NQ, the number of internal coordinates.
   NDD, the number of nonzero experimental frequencies entered with the data. For NDD = 0 no frequencies are entered.
   NZZ, the number of Z matrix elements.
   IFU = 1 suppresses printout of the Z matrix.
   IFW, the L matrix and potential energy distribution suppression option.
   = 1, causes suppression of the printout of the L matrix and potential energy distribution.
   = -1, results in the suppression of the printout of only the potential energy distribution.
   ISKZ, the Z matrix read option.
   = 0, a Z matrix must be entered with the data.
   = 1, the Z matrix from the previous molecule is used.

IFINV, L computation control.
= 0, L is not computed.
= 1, the L is computed.
IFMA = 1 results in suppression of the printout of the L matrix.
IFB, the cartesian displacement coordinate control.
= 1, the B matrix and masses are entered with the input data, and the cartesian displacement coordinates are calculated. IFINV must = 1 for IFB = 1.
= 0, the B matrix and masses are not entered with the input data, and the cartesian displacement coordinates are not computed.
NOAT, the number of atoms in the molecule. NOAT must be entered for IFB = 1.
IFCOR = 1 results in the calculation of the internal mean square amplitude matrix.
NOTEP, designates the number of temperatures for which the cartesian "squared amplitudes" are to be calculated. If NOTEP = 0 the cartesian "squared amplitudes" are calculated for room temperature only.
SCALE, the scale factor for the cartesian displacements. If SCALE = 0.0 the scale factor is assigned a value of 2.0 by the program.
ICAR = 1 results in the suppression of the printout of the cartesian displacement coordinates.
IMSC = 1 results in the suppression of the printout of the cartesian "squared amplitudes" of vibration.
ICOR = 1 results in the calculation of the cartesian coriolis coefficients being bypassed.
ITEMP, the temperature option control for the internal "squared amplitudes" of vibration.
= 0, the computations are completed for a temperature of 0 K.
= 1, the internal "squared amplitudes" are calculated for a temperature of ABST K.
ABST, the temperature in K for which the internal "squared amplitudes" are to be computed.
ICD = 1, description codes identifying the internal coordinates must be entered with the data. These four character codes are printed next to the corresponding "squared amplitudes", potential energy component, or L matrix element to simplify their identification.
IPUN = 1, the "squared amplitudes" and potential energy distribution are written in file EIGV/OUTPUT in the proper format for use as input to SASORT.
IFL = 1, input data for PAM1 is written in file PAM1/DATA.

7. Molecule information card. This line contains the name of the molecule or any other alphanumeric data pertinent to the problem. This line must be included even if blank.

8. Internal coordinate identification cards. If ICD = 1, four character alphanumeric codes must be entered which identify the internal coordinates. The codes must appear in the same order as the internal coordinates which they are representing. Eighteen are typed/line. [FORMAT 18A4].

9. Z matrix. The Z matrix elements are read in as output from UBZM or ZSYM [FORMAT 4(3I3,F9.6)]. The row after the last element must be set equal to -2.

10. The experimental frequencies. If NDD is greater than zero, the experimental frequencies must be entered with the input data. The frequencies are entered in decreasing order 1 through NQ, NDD of which are nonzero. For frequencies which are unknown a zero can be entered.

11. G matrix. The nonzero G matrix elements are entered as output by GMAT [FORMAT 4(2I3,F12.6)]. The row number after the last element must be set equal to -1.

12. The cartesian coordinates. If IFB = 1, the cartesian coordinates must be entered with the input data. The nonzero cartesian coordinates are input as output by CART [FORMAT 4(2I3,F12.6)]. The row number after the last element must be -1.

13. The masses. If IFB = 1, the atomic masses must be entered with the input data in the order 1 through NOAT. The masses are input in free format.

14. B matrix. If IFB =1, the B matrix must be entered with the input data. The B matrix elements are entered as output by CART [FORMAT 4(2I3,F12.6)]. The row number following the last element must be set equal to -5.

15. Data termination card.
    999,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
    If another problem is to be started, the problem ID card of the next problem should be placed at this point.

    Output from EIGV goes to the printer and to files titled EIGV/OUTPUT and PAM1/DATA. The data written to EIGV/OUTPUT is of the proper format for input into SASORT. The data written to PAM1/DATA is formatted for input for PAM1. Output is controlled by variables defined in the molecule control card.

PAMOLE

PAMOLE requires a data file titled PAMOLE/DATA to draw representations of the molecule. The data file must contain the following information:

1. Problem definition card, typed in free format.
   IND,NOAT,NVW,ITITLE,XSTAR,YSTAR,LHGT
   - IND = -09, identifies the problem definition card.
   - NOAT, the number of atoms in the molecule.
   - NVW, the number of views to be drawn of this molecule.
   - ITITLE = 1 permits alphanumeric information to be written on the plotter output.
   - XSTAR, the starting position along the X-axis, in inches from the origin, for the alphanumeric lettering. If ITITLE = 0, XSTAR should be zero.
   - YSTAR, the starting position along the Y-axis, in inches from the origin for the alphanumeric lettering. YSTAR = 0.0 for ITITLE = 0.
   - LGHT, the lettering height in inches. LGHT should be a multiple of 0.07. LGHT = 0.0 for ITITLE = 0.

2. Alphanumeric information. If ITITLE = 1 the alphanumeric labeling to appear on the drawing is included at this point. If ITITLE = 0 a blank line is necessary.

3. BIG. This card requests that the wide paper (29 1/2") be used. The Calcomp 1012 does not handle wide paper so this option is not used, though still available in the program.

4. SCALE XXXX. This card indicates the scale factor to be used in the drawing. If this line is omitted a scale factor of 1 is assumed. 'SCALE' is punched in columns 1-6 and the numerical scale factor in columns 7-10 [FORMAT A4,A2,3F4.0]. The scale factor can be decimal and the Format F4.0 will be overruled.

5. ANGLES , , . This line supplies the angles between the coordinates. α is the angle between the Y- and Z axes, β is the angle between the X- and Z-axes, and γ is the angle between the X- and Y-axes. If this line is omitted rectangular axes are assumed. The word 'ANGLES' is punched in columns 1-6, α in columns 7-10, β in columns 11-14, and γ in columns 15-18 [FORMAT A4,A2,3F4.0]. Again, if decimal numbers are entered the F4.0 format is overruled.

6. SIZES name r name r ... This card gives the general atom names, e.g., C, H, O, Cl, etc., and the corresponding radius of the "ball" representation, r, in atomic units. There can be up to 10 atom names. The word 'SIZES' is typed in columns 1-6, the atom name in column 7-10 and the atom radius in columns 11-13, the remaining atom names and radii follow in groups of 4 and 3 columns through 10 atom names [FORMAT 6X,10(4A1,F3.2)]. The atom names must be left justified.

7. CELL x,y,z. This line gives the fractional coordinates for the atom positions. This option is used when the coordinates are x-ray crystallographic fractional coordinates. The unit cell dimensions are specified in atomic units. If this card is included with the input data all subsequent atom coordinates will be assumed to be fractional. 'CELL' is typed in columns 1-4, x in columns 5-11, y in columns 12-18 and z in columns 19-25 [FORMAT 4A1,3F7.3].

8. Name x y z name1 name2 ... The next set of cards defines the positions of the individual atoms. Each card defines one atom, specifying its name of up to 4 characters in columns 1-4, its position in space by the cartesian or fractional coordinates (x, y, and z are typed in columns 5-11, 12-18 and 19-25, respectively), and the names of the atoms connected to it (up to 8 atoms) typed in four column fields with a blank separating each entry [FORMAT 4A1,3F7.3,8(4A1,1X)]. There should be NOAT cards in this set. The atoms are drawn in the order in which they are defined. The atom names should be left justified.

9. VIEW x y z. The viewpoint(s) are defined next. The view is drawn from a point looking down the line joining the viewpoint to the center of the molecule. The word 'VIEW' is typed in columns 1-4, x is punched in columns 7-10, y in columns 11-14 and z in columns 15-18 [FORMAT 6X,3F4.0]. There should be NVW cards.

10. Data termination card. This card indicates the end of the data deck with a 999 punched in columns 1-3. If another problem is to be included in this data file the problem definition card for the next problem should be placed at this point in the deck.

Atoms that are hidden from view in any drawing are identified in printout to the printer. The program PAM1 can be used to transform the output from EIGV into a form suitable for input to PAMOLE. This aids in depicting the vibrations of the normal modes. In these drawings the arrow heads are drawn in by hand.

PAM1

To convert the cartesian displacement coordinates for the normal vibrations calculated with EIGV into a form usable by PAMOLE, PAM1 requires two data files. One is created by EIGV and is titled PAM1/DATA. The other should be titled PAM1/DATA/1 or otherwise defined in a file statement. This second file should contain the following:

1. Problem definition card, typed in free format.
   IND,NFR,NSFRQ,LLENG,SCALE,NSFR2,NSFR3,XXX,FHEAV,NISO
   - IND = -09, identifies the beginning of a problem.
   - NFR, the number of calculated frequencies.
   - NSFRQ, the number of frequencies to be skipped.
   - LLENG, the minimum displacement vector length.
   - SCALE, the factor for increasing the relative displacement.
   - NSFR2 = 0, a dummy variable.
   - NSFR3, the number of frequencies to skip at the end (e.g., torsions).
   - XXX, a scale factor.
   - FHEAV, a factor for increasing heavy atom displacements relative to hydrogen displacements.
   - NISO, the number of isotopic sets to be processed.

2. The next lines are the same as those required for PAMOLE up to the viewpoint cards. The viewpoint cards are preceded by cards describing the NOAT number of displaced atoms. The input cards of PAMOLE need not contain the proper equilibrium coordinates (these are obtained from the file PAM1/DATA) but the information describing the atoms to which each atom is connected must be correct. The viewpoint cards follow 2(NOAT) atom description cards. These are followed by the data termination card.

   The coordinates and displacements for each normal mode are written the file PAM1/OUTPUT. The entire file can be used as input for PAMOLE or selected modes can be taken from this file.

NFAD

NFAD uses a data file titled NFAD/DATA. If the data file is otherwise titled it must be specified in a file statement. The data file for NFAD must contain the following information:

1. -09, problem ID card.

2. Problem control card. Typed in free format.
   IND,NOPROB,NMOL,NF,IPE
   IND = -09, identifies the start of the problem.
   NOPROB, the number of the problem.
   NMOL, the number of molecules.
   NF, the number of force constants.
   IPE = 1, suppresses the printout of the potential energy distribution.

3. Problem information cards. Three lines containing alphanumeric information about the problem or left blank are required.

4. Force constants. The force constants are read in next in order 1 through NF in free format.

5. Force constant description codes. Four character codes are typed in to identify the force constants. These are typed in order 1 through NF, in four column fields eighteen/line [FORMAT 18A4].

6. Molecule control card, typed in free format.
   IND,NQ,NZZ
   IND = -06, identifies molecule control card.
   NQ, the dimension of the secular equation.
   NZZ, the number of Z matrix elements.

7. Molecule information card. A line containing the name of the molecule or left blank.

8. Z matrix. The Z matrix is input as output by UBZM or ZSYM [FORMAT 4(3I3,F9.6)]. The row number following the last element must be -2.

9. G matrix. The G matrix is input as output by GMAT [FORMAT 4(2I3,F12.6)]. The row number following the last element must be -1.

10. Data termination card.
    999

The potential energy distribution in terms of the force constants is calculated by this program and written both to the printer and to a file titled NFAD/OUTPUT. The file NFAD/OUTPUT is used as an input file for the program FCSORT.

HISTO

The data file for HISTO should be named HISTO/DATA or specified in a file statement. This data file should contain the following information:

1. Problem control card. Typed in free format.
   IND,NMOL,DELT,NBAR
   IND = -09, identifies beginning of the problem.
   NMOL = 2
   DELT, the number of data units per inch of axis.
   NBAR, the number of bar graphs/page.

2. X-axis label. Any alphanumeric information.

3. Labels for each of the bar graphs. One/line, NBAR are required.

4. Label for the figure. Any alphanumeric information describing the overall figure.

5. Molecule control card, typed in free format.
   IND,FIRST,ALEN,NF(1),...,NF(NBAR),NC
   IND = -06, identifies the molecule control card.
   FIRST, the starting value of the X-axis.
   ALEN, the length of the axis.
   NF( ), the number of points on each of the NBAR graphs.
   Input NBAR values.
   NC, the number of points to be connected between graphs.

6. Frequencies. The frequencies in each of the NBAR arrays. These should be input in the same order as their titles.

7. Molecule control card. The next molecule control card is placed at this point. This card would be followed by the NBAR arrays. The data termination card (999) could also be placed in this position.

FCSORT

The program FCSORT requires two data files. One is created by the program NFAD and contains information on the potential energy distribution of the normal modes in terms of the force constants. This file is titled NFAD/OUTPUT. The second file required is titled FCSORT/DATA or otherwise specified in a file statement. This second data file must contain the following:

1. Problem control card, typed in free format.
   IND,NOPROB,NF,NFR,ND
   IND = -09, identifies the problem control card.
   NOPROB, the problem number.
   NF, the number of force constants.
   NFR, the number of frequencies.
   ND, the number of diagonal force constants.

2. Force constant descriptions. Four character descriptions of the force constants are input in four column fields, eighteen per line [FORMAT 18A4].

3. Diagonal force constants. The numbers of the diagonal force constants are read in next. The ND values are input in free format.

4. Problem information lines. Two lines containing alphanumeric information or left blank are required.

5. Data termination card.
   999

The potential energy distributions are written out to the printer.

PESORT

PESORT requires two data files. One is created by EIGV and contains information on the potential energy distribution of the molecule. This file is titled EIGV/OUTPUT. The second data file is titled PESORT/DATA and requires the following information:

1. Problem control card, typed in free format.
   NT,NF,NQ
   - NT, the number of kinds of internal coordinates.
   - NF, the number of frequencies.
   - NQ, the number of internal coordinates.

2. The number of internal coordinates of each kind. NT numbers are required.

3. Internal coordinate descriptions. Four character descriptions of the internal coordinates are required. These are input in four column fields, eighteen/line. The descriptions should be right justified.

4. Title for the table. Or any other alphanumeric information you may wish to have written at the top of the table.

5. Observed frequencies. NQ observed frequencies are input in decreasing numerical order, in free format.

All output from this program goes to the printer.